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# CHEMICAL EXAMINATION OF THE FATTY OIL FROM THE SEEDS OF *MALLOTUS PHILIPPINENSIS* MUEL.-ARG.

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In 1936 Krishna[1], *et al.*, drew attention to the drying properties of the fatty oil from the seed kernels of *Mallotus philippinensis* Muel.-Arg. (Fam. Euphorbeaceæ) commonly known as " Kamala " or " Kamela " in Hindi and as " Rohini " or " Raini " in Kumaon and Dehra Dun Districts of Uttar Pradesh. In 1941 and 1942 the results of the preliminary chemical examination of the fatty oil were published in the Annual Reports[2] of the Forest Research Institute and Colleges. This was soon followed by the notes of Singh and Saran[3] and Puntambekar,[4] the latter worker pointing to the highly drying nature of the oil comparable to that of tung Oil. In this laboratory further work was suspended during the remaining period of the World War II but the study of the component acids of the oil was again resumed in early 1946 and the results reported in the subsequent Annual Reports[5] of this Institute. In 1948 Aggarwal,[6] *et al.*, published their first paper on the chemical examination of the fatty oil giving a different picture of its chemical composition. This was followed in 1949 by a paper from Bhushan and Om Prakash[7] on the chemical and physical characteristics of the oil as well as its performance as a fast drying oil when used alone or in combination with double boiled linseed oil. The recent letter by Aggarwal,[8] *et al.*, gives the possible structural formulæ for Kamlonic acid, the active component conjugated double bond acid, isolated by them from the oil. In view of the different findings of the author to that reported by Aggarwal, *et al.*, it is now thought desirable to put together the findings from this laboratory.

The black seeds from the fruit of Kamala were found to contain 22 to 24 per cent. of a pale bland viscous oil having medicinal properties but they were mostly treated as a waste product in the preparation of Kamala powder of trade. The oil could not be expressed from the kernel in a hydraulic press probably on account of its viscous nature and tendency to polymerise owing to the effect of heat, pressure, air and light. It was, therefore,

extracted from the fresh seed kernels with petroleum ether, sulphuric ether and benzene with the following results:

| Solvent | Colour | Consistency | Yield in kernels | Behaviour on standing |
|---|---|---|---|---|
| 1 Petroleum ether .. | Reddish brown | Thick liquid | 50% | |
| 2 Sulphuric ether .. | do | Viscous liquid or solid | 50% | |
| 3 Benzene .. | Dark brown | Very viscoas | 61% | Becomes solid & hard and insoluble in the solvents for fatty oils. |

Samples of the fat extracted with sulphuric ether and kept in sealed bottles in a refrigerator were found to be practically unaffected after one year.

It has been found that the oil exposed to atmosphere in a thin film changes to a rubbery mass at room temperature (30°) within 48 hours. The effect is quite rapid if the oil or its mixed fatty acids are heated either alone or with chemicals like acetic anhydride and lead acetate. Thus in the determination of acetyl value and separation of solid and liquid acids by the Twitchell's method the oil and its fatty acids have been found to get altered partially to leathery products. The change appears to be a progressive one particularly in case of the mixed fatty acids which in contact with air get altered to a hard insoluble product from the exposed surface to the interior. During conversion of the acids to their lead salts and separation of the latter from alcohol into alcohol-soluble and alcohol-insoluble salts as much as 20% of the acids when liberated from them were found to have become rubbery. Since the oil shows a high refractory index (1·5105), a high iodine value (183), a significant diene value (42) and an appreciable carbonyl value (26) and is four times as fast jellying as tung oil not only the presence of a conjugated system of double bonds in the component acids is indicated but also an additional factor of activity in the structure of the fatty oil and acids. It has been noted that mixtures of the oil in other drying, semi-drying and non-drying oils like linseed, olive, castor, coconut, cocobutter, etc., as well as with solvents like benzene, toluene, xylene, turpentine, etc., when heated react and set to gels, indicating addition of the conjugated system of double bonds of the Kamala oil to the double bonds of the glycerides, benzene, toluene, xylene, turpentine, etc. This is a very significant property of the oil suggesting many practical applications.

In the study of the component fatty acids of this highly reactive oil, the problem has been now actually to isolate them without altering their

nature and structure. The fatty oil was kept in bottles tightly corked and sealed with paraffin wax and stored in a refrigerator. The following procedures for the separation and identification of individual acids were adopted:

(*a*) The mixed acids were separated mainly into "solid acids" and "liquid acids" by the modified Twitchell's method.[9] The solid acids which contained almost all the polythenoid conjugated acids were isolated and identified by fractional crystallization from different solvents and catalytic hydrogenation of the different fractions. The permanganate oxidation products of solid acids in acetone were also studied.

The liquid acids were identified by their permanganate oxidation and bromination products.

(*b*) The mixed acids were reacted with maleic anhydride to form adducts with the conjugated polyethenoid acids present in them; after the removal of the adducts the components of the residual acids were studied.

This study has indicated that the component acids are mostly unsaturated acids mainly conjugated polyethenoid $C_{18}$ (probably isomeric-eleostearic and isomeric keto-linoleic acids) oleic and linoleic acids and to a small extent saturated acids, namely, stearic and lower acids. Although valeric and undecylic acids have been identified in the products of permanganate oxidation of the solid unsaturated acids, the position of conjugated double bonds yet remains to be finalized and that of the keto group in the isomeric keto linoleic or isomeric keto-eleostearic acid still remains indefinite. In this connection attention might be drawn to the different picture with respect to the component acids presented by Aggarwal, *et al.*[6,8] They have found the principal unsaturated acid to be Kamlonic acid (isomeric oxy-eleostearic acid) and that the oxy group is not a keto but a hydroxyl one occupying the ($\omega$) position and having only two double bonds conjugated. Further, instead of stearic, oleic and linoleic acids they have reported the presence of palmitic and myristic acids but have not supplied confirmatory data to prove their occurrence.

## Experimental

The air-dry fruit consisted of the pericarp with the outer thin layer of Kamala powder (70·9%) and the black seed (29·1%). The seed in its turn consists of 53% testa and 47% kernel, the latter of which yields 50% of a viscous or solid fatty oil when extracted with solvents like petroleum ether, benzene, sulphuric ether, etc.

The characteristics of the fat extracted with petroleum ether are recorded below along with the values obtained by other workers:

| | Author | Singh & Saran | Aggarwal, *et al.* | Bhushan & Om Prakash |
|---|---|---|---|---|
| Sp. gr. at 30° C. | 0·9347 | 0·9933 | 0·9409 | 0·9444 |
| Ref. index at 30° C. | 1·5105 | 1·5155 | 1·5052 | .. |
| Unsaponifiable matter | 1·75 | 1·9 | 1·7 | 2·3 |
| Viscosity | .. | .. | 386·3 @ 40° C. | .. |
| Acid value | 5·7 | 11·3 | 6·4 | 5·2 |
| Saponification value | 178·3 | 207·6 | 195·0 | 190·7 |
| Iodine value | 183·2 (Hanus) | 157·3 | 179·8 (Woburn "B") | 166·4 (Wijs) |
| Acetyl value | 49·24 | 46·8 | 15·7–44 | .. |
| Carbonyl value | 26·0 | .. | .. | .. |
| Diene value (Maleic anhydride value) | 42·9 | .. | 40·4 | 48·5 |
| Browne heat test | 2′ | .. | 9′ 30″ | .. |

## COMPOSITION OF THE MIXED ACIDS

200 g. of the fat was saponified in the usual manner with alcoholic sodium hydroxide. On distilling off the alcohol at 70° under vacuum the resultant soap was dissolved in 2 litres of water and the solution extracted for the unsaponifiable matter with sulphuric ether. The ether extracted soap solution was then carefully treated with con. hydrochloric acid, warmed up to 70° and the liberated mixed acid separated from the lower watery layer. The mixed acids were taken up in sulphuric ether, washed with water dried over anhydrous magnesium sulphate and the ether distilled off.

## CHARACTERISTICS OF THE MIXED ACIDS

| | 1 | 2 | 3 | 4 |
|---|---|---|---|---|
| Melting point | 51–52° C. | .. | 45·5° C. | 49·5° C. |
| Mean molecular wt. | 300·6 | .. | 281·2 Calc. from neutralisation value (199·5) obtained by these authors. | .. |
| Iodine value | 168·0 (Hanus) | .. | 182·7 (Woburn "B") | .. |
| Diene value (Ellis & Jones) | 58·0 | .. | 56·6 | .. |
| Carbonyl value | 60·0 | .. | .. | .. |

100 g. of the acids of the above characteristics were subjected to Twitchells lead-salt-alcohol separated with the following results:

"Liquid" acids .. 31%; i.v. 87–97.

"Solid" acids .. 49%; I.V. 120–140.

Polymerised acids .. 20%.

## Liquid Acids

*Oxidation.*— A portion of the liquid acids was converted into potassium soaps and oxidised in cold alkaline solution with dilute potassium permanganate according to the modified method of Hazura.[10] From the precipitated oxidized acids only dihydroxy stearic acid M.P. 131–32°, m.w. 314, has been isolated.

*Bromination.*—Freshly prepared liquid acids were brominated according to the method of Eibner and Muggantheler[11] but no insoluble hexa or higher bromides were obtained. The brominated acids (Br, 37·56%) were then crystallised from petroleum ether (b.p. 40°–60° C.) when white needles (m.p. 113°–14° C.) were obtained. These were evidently tetrabromostearic acid and were confirmed as such by their mixed melting point with an authentic sample of the tetrabromide.

Formation of dihydroxy stearic and tetra bromostearic acids and the iodine value of the liquid acids show that they consist of mainly oleic acid (92%) and a small quantity of linoleic acid (8%).

## Solid Acids

A freshly prepared sample of solid acids (i.v. 140) on exposure to air soon became resilient and insoluble in the organic solvents indicating their great tendency to polymerize due to high unsaturation. The usual process of converting them into methyl esters and separating the latter into pure components by fractional distillation under vacuum could not be employed as heat readily polymerised them. Therefore, they were successively extracted and crystallized at room temperature in an atmosphere of $CO_2$ from petroleum ether (b.p. 40°–60° C.) and benzene and separated into the following fractions:

| Fractions | Solvents | Yield |
|---|---|---|
| (*a*) | Crystals from petroleum ether m.p. 77–78° C. (m.w. 281) .. | 25% |
| (*b*) | Crystals from benzene m.p. 77–78° C. (m.w. 286) .. .. | 55% |
| (*c*) | Polymerised product insoluble in benzene .. .. | 10% |
| (*d*) | Viscous oil from mother liquor of (*a*) .. .. .. | 5% |
| (*e*) | Viscous oil from mother liquor of (*b*) .. .. .. | 5% |

The fractions (*a*) and (*b*) were mixed together, dissolved in 95% alcohol and reduced with hydrogen at room temperature in the presence of active platinum oxide catalyst[12] for three hours. After the removal of the catalyst by filtration the products of reduction were isolated on concentration of the alcoholic solution as follows;

(1) Crystals (40%) m.p. 93–94° C., i.v. 9, m.w. 305, acetyl derivative m.p. 79–80° C. (Found: C, 71·5%; H, 11·7%; calculated for hydroxy saturated $C_{18}$ acids $C_{18}H_{36}O_3$, C, 72·0; H, 12·0%).

(2) Crystals from mother liquor (15%), m.p. 69–70°, mixed melting with an authentic sample of stearic acid remained unchanged.

(3) Dark reddish brown liquid acids (45%) from the mother liquor of (2) i.v. 80, m.v. 280, indicating most of the material to be an isomer of oleic acid obtained as the result of partial reduction of conjugated system of double bonds of isomeric eleostearic acid.

Fraction (*c*) being insoluble in organic solvents was not worked up further; fractions (*d*) and (*e*) being almost similar were mixed together and the mixture on further hydrogenation gave a small quantity of acids (i.v. 8, m.w. 267) melting at 55° C. to 56° C. indicating mixtures of stearic acid with some lower saturated acids.

It will thus be seen from the above data that the mixed acids consist of 31% of liquid acids (oleic and linoleic acids) and 69% of solid acids mostly $C_{18}$ polyethenoid acids (i.v. over 120) which as a result of undergoing Twitchell's separation gets converted to an extent of 20% to a hard polymerised product insoluble in organic solvents. The remaining 49% besides the multiple double bonds contain oxygen in the molecule and during its fractional separation from solvents gets further polymerised to the extent of 10%. The unpolymerised polyethenoid and oxygen containing acids on catalytic reduction yield an oxy-stearic acid isomer, m.p. 93–94° C., stearic acid, m.p. 69–70° C., an iso-oleic acid (i.v. 80, m.d. 280) and small quantities of saturated acids lower than stearic acid. The above data on calculation gives the following composition of the mixed acids:

| | |
|---|---|
| Oleic acid .. .. .. .. .. | 28·6% |
| Linoleic acid .. .. .. .. | 2·4% |
| Polyethenoid keto $C_{18}$ acid .. .. .. | 15·7% |
| Isomeric eleostearic acid .. .. .. | 23·5% |
| Saturated acids .. .. .. .. | 4·9% |
| Polymerised acid .. .. .. .. | 24·9% |

Since the liquid acids have not been found to polymerise at any stage and since the solid acids have actually yielded 10% of polymerised acids during their fractional crystallization the polymerisation undergoing constituents evidently are located in the solid acids and no doubt are the conjugated polyethenoid keto $C_{18}$ and isomeric eleostearic acids found in them. The polymerised acids can, therefore, be taken to have the same proportionate composition in the unpolymerised state as is represented by poly-ethenoid

keto $C_{18}$ and isomeric eleostearic acids in the above table for the composition of the mixed acids. Taking these facts into consideration the composition of the total mixed acids in the unpolymerised state works out as follows:

| | |
|---|---|
| Oleic acid .. .. .. | 28·6% |
| Linoleic acid .. .. .. | 2·4% |
| Polyethenoid keto $C_{18}$ acid .. | 25·7% |
| Isomeric Eleostearic acid .. | 38·4% |
| Saturated acids .. .. .. | 4·9% |

Oxidation of the solid unsaturated acids in acetone solution with potassium permanganate, removal of acetone by distillation and reduction of the excess permanganate and manganese dioxide with sodium sulphite and sulphuric acid gave a mixture of fatty acids, on steam distillation of which a volatile acid was obtained and was identified as valeric acid (m.w. 99). The residual mixture of fatty acids on extraction with sulphuric ether and crystallization of extract from dilute acetone in cold yielded a product (m.w. 187·5) which was identified as undecylic acid (m.w. 186). No other compound could be isolated in a pure condition.

In the light of the above findings the polyethenoid keto $C_{18}$ acid and the isomeric eleostearic acid present in the solid acids would respectively appear to have the following possible structural formulæ:

either

(1) (*a*) $CH_3-(CH_2)_9-CH=CH-CH=CH-CH_2-\overset{\overset{O}{\|}}{C}-CH_2-\overset{\overset{O}{\|}}{C}-OH$

(isomeric keto-linoleic acid)

(*b*) $CH_3-(CH_2)_3-CH=CH-CH=CH-CH=CH-(CH_2)_7\overset{\overset{O}{\|}}{C}-OH$

(eleostearic acid)

or

(2) (*a*) $CH_3-(CH_2)_3-CH=CH-CH=CH-CH=CH-\overset{=O}{C}-(CH_2)_6-\overset{\overset{O}{\|}}{C}-OH$

(keto-eleostearic acid)

(*b*) $CH_3-(CH_2)_9-CH=CH-CH=CH-CH=CH-CH_2-\overset{\overset{O}{\|}}{C}-OH$

(isomeric eleostearic acid)

The components of the mixed acids have also been found from the procedure adopted for determination of the diene value by the following way:

The mixed acids were treated with maleic anhydride in toluene solution according to the method of Ellis and Jones.[13] The toluene ether solution of the adduct after the removal of the unreacted maleic anhydride with hot water in a separatory funnel was evaporated on a hot water-bath to remove the solvents. The residual adduct was extracted with petroleum ether to remove all the fatty acids (i.v. 82·0) unreacted with maleic anhydride. Then knowing the diene value (58) the composition of the mixed acids works out and compares with the above recorded composition (Twitchells method) as follows:

| | | Twitchells method |
|---|---|---|
| Conjugated double bond acids .. | 66·0% | 66·5% |
| Oleic acid .. .. .. | 30·0% | 28·6% |
| Saturated acids .. .. .. | 4·0% | 4·9% |

## DISCUSSIONS

1. It has been found that the conjugated polyethenoid glycerides and acids dissolved in solvents containing double bonds in the molecule such as benzene, toluene, xylene and turpentine react with the solvents on prolonged standing or heating. The significantly high yield of the fatty oil extracted with benzene, *viz.*, 61% as compared with 50% obtained by petroleum or sulphuric ether extracted oil is due to this effect. Benzene has simply reacted with the conjugated polyethenoid glycerides of the oil and the resulting adduct remains behind on removal of benzene and thereby increases the weight of the oil. Petroleum ether or sulphuric ether extracted oil does not behave in this way.

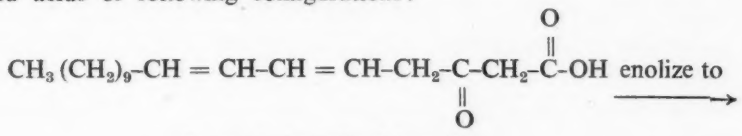
2. The family relationship and the similarity of properties between Kamala and tung oils, which indicates similarity of their chemical composition, is worth noting. Both the oils are derived from the seed kernels of small trees belonging to the same botanical family, *Euphorbeaceæ*. Both have high refractive indices. Both gelatinize rapidly at high temperatures (Browne heat test). Within 48 hours at room temperature in the absence of driers both give films that are opaque, matt and dull producing the typical wrinkled effect. Bodied with linseed oil or with resins both give waterproof varnishes of high gloss and covering power. Both contain about 70% glycerides of conjugated polyethenoid $C_{18}$ acids.

3. The facts that the conjugated polyethenoid acids occurring in "solid" acids are reduced with catalytic hydrogen to hydroxy stearic acid isomer and to an isooleic acid and the latter on further catalytic reduction is reduced to stearic acid indicate that they contain polyethenoid keto $C_{18}$

and isomeric eleostearic acids. The presence of the former acid is further corraborated by the carbonyl value (60) of the mixed acids.

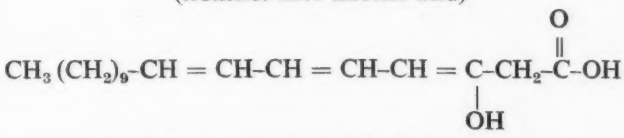
4. Browne's heat test has shown that Kamala oil becomes solid in 2 minutes as compared with 8½ minutes taken by tung oil. This fact considered with the component glycerides of the two oils point to the higher reactive nature of the component glycerides of kamala oil than those of tung oil. Whereas tung oil has been reported to contain 70% glycerides of eleostearic acid, kamala oil has been found to contain nearly the same total percentage of the glycerides of polyethenoid keto $C_{18}$ and isomeric eleostearic acids. In other words a mixture of the glycerides of these two conjugated polyethenoid acids is found to be more reactive than the same concentration of glycerides of eleostearic acid alone. This behaviour leads to the possible inference that the mixture is more reactive because the intermolecular reaction between the two different conjugated polyethenoid glycerides of Kamala oil is catalysed by the oxygen of one of the glycerides. This effect is naturally absent in tung oil which provides no such catalytic component.

5. The structures (1) *a* (isomeric keto-linoleic acid) and (1) *b* (eleostearic acid) proposed for the polyethenoid keto $C_{18}$ acid and isomeric eleostearic acid appear to be more likely than (2) *a* and (2) *b* since the common family relationship of kamala and tung oils would indicate that what has been considered as isomeric eleostearic acid is really eleostearic acid. This inference is further supported by the identification of n-valeric acid in the products of permanganate oxidation. The keto acid having two active methylene groups adjacent to the carbonyl group is readily susceptible to enolizing in presence of catalyst or heat and to produce highly reactive conjugated acids of following configurations:



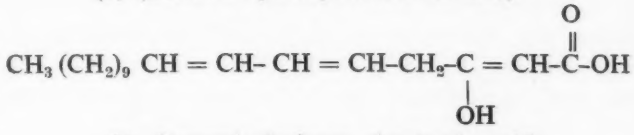
(isomeric keto linoleic acid)

either



(P) (isomeric hydroxy eleostearic acid)

Or



(R) (Isomeric hydroxy eleostearic acid)

The (P) form is expected to be the more reactive than the (R) form as it contains the 3rd double bond in conjugated position. This structure (1 *a*) therefore is in keeping with the finding of undecylic acid in the products of permanganate oxidation of " solid " acids.

6. The main points of difference between the findings of Aggarwal, *et al.*, and the author are as follows:

| | Aggarwal, *et al.* | Author |
|---|---|---|
| I. | No carbonyl value exhibited by the oil or its mixed acids. | Carbonyl values[14] exhibited by the oil and its mixed acids. |
| II. | Occurrence of Kamlonic acid or (w) hydroxy isomeric eleostearic acid, α-form, m.p. 77–78°, β-form m.p. 86–87°, m.w. 293·5, which on catalytic reduction gives (w) hydroxy stearic acid, m.p. 100·5° C., m.w. 305, acetyl derivative m.p. 72° C. | Occurrence of a mixture of (x) keto polyethenoid $C_{18}$ acid and isomeric-eleostearic acid (crystals from the petroleum-ether; m.p. 77–78°, m.w. 281, and crystals from benzene, m.p. 77–78°, m.w. 286) which on catalytic reduction and crystallization from alcoholic solution give (x) hydroxy isomeric stearic acid (m.p. 93–94° C., m.w, 305, acetyl derivative 79–80° C.) and stearic acid (m.p. 68–69° C, m.w. 285) respectively. |
| III. | Browne heat test 9′ 30″. | 2′. |
| IV. | Out of the three double bonds of Kamlonic acid only two in conjugated position. | All the three double bonds of (x) keto polyethenoid $C_{11}$ acid and isomeric eleostearic acid in conjugated position. |

7. Aggarwal, *et al.*, have so far advanced no direct proof for the presence of OH group in the (ω) position in " Kamlonic " acid, *i.e.* (ω) hydroxy isomeric-eleostearic acid although its presence is just indicated by the erratic acetyl values (15–44) reported by them for the oil. The only proof they offer is its reduction to hydroxystearic acid by catalytic reduction. On the other hand carbonyl values shown both by the oil and its mixed acids strongly indicate the presence of a keto group in (x) position in one of the conjugated acids actually present initially in the mixed acids. It might be pointed out that Aggarwal, *et al.*, converted the original α-Kamlonic acid (m.p. 77–78° C.) which corresponds to the author's (x) keto polyethenoid $C_{18}$ acid to β-Kamlonic acid (m.p. 86–87; m.w. 293·5) by irradication under ultra-

violet light. That is they have used a well-known isomerisation process to alter the constitution of the original acid and later supplied the proof of its structure by catalytic reduction of the isomerised acid. Why could not the α-form be reduced directly to the hydroxy stearic acid stage? In the present case it is likely that the isomerisation, after the ketol enol tautomerisation analogy, has also tautomerised the original carbonyl group to the hydroxyl.

8. From the data presented by Aggarwal, *et al.*, it will be seen that the mixed acids have the following composition:

| | | |
|---|---|---|
| *Kamlonic acid* | .. | 50%, i.v. 249·6. |
| Other unsaturated acids | .. | 38%, i.v. (X), m.m.w. (Y). |
| Saturated acids | .. | 12%, i.v., nil, m.m.w., 247. |
| The total mixed acids | .. | 100%, i.v. 182·7, m.m.w., 281·2. |

Since the constants (iodine value and m.m.w.) for the Kamlonic acid and the saturated acids have been determined by them the same for the other unsaturated acids can be calculated and have been found to be i.v. (X) = 152 and m.m.w. (Y) = 267·7. The acids with these values would indicate a mixture of $C_{16}$ and $C_{18}$ multiple double bond acids. These, however, have so far not been reported. As a matter of fact no data has been so far published by them for the 38% of these unsaturated acids.

9. In view of the above different findings by Aggarwal, *et al.*, and the author it now becomes necessary to study the absorption spectra of the individual as well as the mixed acids of kamala oil to clarify their structure.

## Unsaponifiable Matter

The unsaponifiable matter isolated from the saponified oil (sodium soap) by extraction with sulphuric ether before liberation of the mixed acids was crystallized thrice from concentrated alcohol yielding crystal melting at 131–32° C. (acetate m.p., 129–30° C.). The sterol has a specific rotation of −35·99° C. (Conc. 0·139%) in chloroform and appears to be the common phytosterol, sitosterol, found in fatty oils of vegetable origin.

## Summary

1. Kamala oil is one of the lesser known indigenous oils of forest origin and perhaps the most rapid drying oil, even faster than tung oil, among those so far known to science.

2. In contact with air and at laboratory temperature it rapidly polymerises to a hard mass insoluble in organic solvents.

3. It consists of the glycerides of isomeric-eleostearic, (x) keto polyethenoid $C_{18}$, oleic, linoleic, stearic and lower saturated acids.

4. The rapid drying nature of the oil is due to the presence of the glycerides of (x) keto polyethenoid $C_{18}$ and isomeric-eleostearic acids.

5. The unsaponifiable matter of the fatty oil has yielded the common phytosterol, sitosterol, m.p. 131–32° C. (acetate, m.p. 129–30° C.).

## REFERENCES


1. Krishna, S., Puntambekar, S. V. and Raizada, M. B. — *Indian Forest Record* (New Series) 1936, **1** (1), 2.
2. *Forest Research in India & Burma*, 1940–41, Pt. I, 112 and 1941–42, Pt. I, 92–93.
3. Singh, B. K. and Saran, B. .. *Current Science*, 1942, **11**, 360.
4. Puntambekar, S. V. .. *Ibid.*, 1942, **11**, 464.
5. *Forest Research in India & Burma*, Pt. I, 1946–47, p. 72.
   .. *Ibid.*, Pt. I, 1947–48, pp. 65 & 66.
   .. *Ibid.*, ,, 1948–49, in press.
   .. *Ibid.*, ,, 1949–50, in press.
   .. *Ibid.*, ,, 1950–51, in press.
6. Aggarwal, J. S., Bhatnagar, S. S., Parkash Narain and Karimulla — *J. Sci. & Industr. Res.*, 1948, **7** (9), 136.
7. Bhushan, D. and Om Prakash, A. R. — *Proceedings of the Fifth Annual Convention of the Oil Technologists Association, India, Kanpur*, 1949, 39.
8. Gupta, S. C., Sharma, V. N. and Aggarwal, J. S. — *J. Sci. & Ind. Res.*, 1951, **10 B** (3), 76.
9. Hilditch, T. P. .. *The Chemical Constitution of Natural Fats*, 1940, 371.
10. Lewkowitch, J. .. *Chemical Technology and Analysis of Oils, Fats & Waxes*, 6th Edition, (1922), **1**, 575.
11. ———— .. *Ibid.*, 585.
12. Adams, R., Voorhus, V. and Shriner, R. L. .. *Organic Synthesis*, 1928, **8**, 92.
13. Ellis, B. A. and Jones, R. A. .. *Analyst*, 1936, **61**, 814.
14. Kaufmann, M. P., *et al.* .. *Fatte u Selfen*, 1938, **45**, 616;
    Trozzols, A. H. and Licber, E. .. *Analytical Chemistry*, 1950, **22**, 764.

# OXIDATION BY CHLORAMINE-T

## Part II. Redox Potential of Chloramine-T—Sulphonamide Systems

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In connection with the study[1] of the oxidation of hydrogen sulphide by chloramine-T, it was deemed necessary to determine the effect of pH on the redox potential of chloramine-T—sulphonamide systems.

When chloramine-T was acidified, there was turbidity due to the separation of dichloramine-T. Whether the formation of this sparingly soluble substance had any effect on the potential was also determined. Dichloramine-T was prepared from chloramine-T by treatment with cold sodium hypochlorite. The purity of the dichloramine-T was determined by estimation of (*a*) available oxygen (iodometrically) and (*b*) Nitrogen (by Micro-Kjeldahl method). The purity of the substance was found to be 99·6% by the first method and 99·8% by the second.

The chloramine-T and the sulphonamide (M.P. 137° C.) employed were also of high purity. The potentials were determined in 0·2 N solutions of chloramine-T containing sulphonamide in excess. Various types of electrodes were tried. A saturated calomel electrode was used in combination with the redox half cell.

### Experimental Results

Table I

*Effect of Dichloramine-T on the Redox Potential*

| 1<br>Sl. No. | 2<br>pH | 3<br>Buffer used | 4<br>System | 5<br>Redox potential in volts |
|---|---|---|---|---|
| 1 | 0·65 | Sodium acetate-hydrocloric acid | (Chloramine-T saturated with sulphonamide) | 1·139 |
| 2 | 0·65 | do | do + dichloramine-T | 1·139 |
| 3 | 7·0 | Phosphate | (Chloramine-T saturated with sulphonamide) | 0·778 |
| 4 | 7·0 | do | do + dichloramine-T | 0·778 |
| 5 | 9·2 | Borax | (Chloramine-T saturated with sulphonamide) | 0·614 |
| 6 | 9·2 | do | do + dichloramide-T | 0·615 |

* This investigation was conducted at Central College, Bangalore and formed part of the thesis of A. R. V. accepted for the M.Sc. Degree of the Mysore University.

TABLE II

*Redox Potential with Various Types of Electrodes*

| 1 Sl. No. | 2 pH | 3 Buffer | 4 Electrode | 5 Redox potential in volts |
|---|---|---|---|---|
| 1 | 0·65 | Sodium acetate-hydrochloric acid | Bright platinum | 1·138 |
| 2 | 0·65 | do | Platinum black | 1·139 |
| 3 | 0·65 | do | Tungsten | 1·139 |
| 4 | 0·65 | do | Silver | 1·139 |
| 5 | 0·65 | do | Gold | 1·139 |
| 6 | 2·64 | do | Platinum bright | 0·946 |
| 7 | 2·64 | do | Platinum black | 0·945 |
| 8 | 4·76 | do | Platinum bright | 0·834 |
| 9 | 4·76 | do | Platinum black | 0·835 |
| 10 | 7·0 | Phosphate | Platinum bright | 0·778 |
| 11 | 7·0 | do | Platinum black | 0·778 |
| 12 | 7·0 | do | Platinum bright + osmic acid | 0·778 |
| 13 | 7·0 | do | Plantinum bright + 2 ml. sodium molybdate (5%) | 0·777 |
| 14 | 7·0 | do | Platinum bright + 2 ml. sodium tungstate (5%) | 0·778 |
| 15 | 9·2 | Borax | Platinum bright | 0·615 |
| 16 | 9·2 | do | Platinum black | 0·614 |
| 17 | 12 | Borax-sodium hydroxide | Platinum bright | 0·500 |
| 18 | 12 | do | Platinum black | 0·499 |
| 19 | 12 | do | Tungsten | 0·499 |
| 20 | 12 | do | Silver | 0·499 |
| 21 | 12 | do | Gold | 0·499 |

*Redox system*: 0·2 *N chloramine-T saturated with sulphonamide*

TABLE III

*Solubility of* p-*Toluene Sulphonamide at* 25° *C.*

| 1 Sl. No. | 2 pH | 3 Buffer | 4 g. per litre of the saturated soln. |
|---|---|---|---|
| 1 | 0·65 | Sodium acetate-hydrochloric acid | 1·150 |
| 2 | 4·76 | do | 2·102 |
| 3 | 7·0 | Phosphate | 3·019 |
| 4 | .. | Water | 3·15 |
| 5 | 9·2 | Borax | 4·266 |
| 6 | 12 | Borax-sodium hydroxide | 5·821 |

## DISCUSSION

The results show that the redox potential of chloramine-T-sulphonamide system is influenced by the pH of the solution. The influence of pH on the potential may be attributed to the increase in solubility of the sulphonamide as the pH rises. The solubility of sulphonamide at various pH

values was determined by the estimation of nitrogen (Micro-Kjeldahl) in aliquots of the saturated solution.

The nature of the electrode seems to have no effect on the potential difference. From this, it may be concluded that the potential differences measured are real redox potentials.

In our paper on the oxidation of hydrogen sulphide by chloramine-T, it has been pointed out, that with an increase in pH, sulphate production diminishes, while oxidation of hydrogen sulphide to sulphur increases in magnitude. The decrease in redox potential with rise in pH would no doubt account for this. But the experimental results cannot be fully explained on the basis of redox potential. For, while the redox potential of chloramine-T is not affected by the presence of osmic acid, sodium molybdate or sodium tungstate, these reagents have a marked effect on the relative proportion of sulphate and sulphur formed during the oxidation of hydrogen sulphide by chloramine-T. The molybdate increases sulphate formation while the other two reagents depress it.

The specific influence of these reagents on the oxidation of hydrogen sulphide, while the redox potential is unaffected, can be accounted for on the basis of the catalytic effect of each of these reagents on dihydrogen sulphoxide, the primary product of oxidation of hydrogen sulphide. The reagents probably influence the decomposition of the sulphoxide to sulphur and water, as also the further oxidation of the sulphoxide to sulphate, by chloramine-T.

## Summary

Potentials of the chloramine-T—sulphonamide system have been found to be real redox potentials. With an increase in pH, the oxidation potential decreases. Depending on the pH of the solution, the oxidation of hydrogen sulphide by chloramine-T yields varying proportions of sulphur and sulphate. Reagents like osmic acid, sodium tungstate and sodium molybdate are also found to affect the ratio of sulphur to sulphate, formed by the oxidation of hydrogen sulphide.

A complete explanation for the observed results cannot be based on the effect of pH on the redox potential, as these reagents do not alter the potential. The specific effect of these reagents is probably due to their influence on dihydrogen sulphoxide, the primary product of oxidation of hydrogen sulphide.

## Reference

1. Vasudeva Murthy, A. R. and Sanjiva Rao, B. .. *Proc. Ind. Acad. Sci.*, 1952, **35**, 7.

# A NOTE ON THE DETERMINATION OF RESACETOPHENONE BY KOPPESCHAAR'S METHOD

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There is a large volume of literature[1,2,3] on the quantitative bromination of phenols and phenolic compounds. Phenol itself is readily and quantitatively tri-brominated but substituted phenols frequently yield erratic results. The chief factors involved are: (*a*) nature and position of substituent, (*b*) amount of bromine added in excess, (*c*) temperature, and (*d*) acid concentration. No universal bromination procedure could therefore be laid down for the estimation of phenolic compounds. The titration of resacetophenone with standard bromate-bromide mixture in presence of mineral acid (Koppeschaar's method) was now investigated and the results reported. The ketone was dissolved in acetic acid and the titrations performed in an all-glass apparatus designed to prevent loss of bromine.

Brominations were carried out at laboratory temperature (ca. 30° C.) with varying amounts of bromate-bromide mixture added initially. The acid concentration employed was approximately 1 N in all the experiments. The excess of bromate was determined by adding potassium iodide and titrating the liberated iodine with standard sodium thiosulphate using starch as indicator. The volume of bromate used up was calculated in the usual manner. The results are given in Table I.

The results presented in Table I show that the bromate used up does not depend on the amount of ketone alone but also on the magnitude of the excess bromate used initially. Consequently reproducible results could not be obtained in a direct titration by Koppeschaar's method. However, on plotting the total volume of bromate solution initially added against the actual excess in each experiment (determined iodometrically) a linear relationship was observed.

By extrapolation to zero excess, the bromate equivalents of the ketone in solution were obtained. These values corresponded to di-bromination. Typical results obtained are given in Table II.

TABLE I

| Resacetophenone taken (gm.) | Bromate (c.c.) | |
|---|---|---|
| | Initially added | Used up |
| 0·0226 | 5·0 | 4·82 |
| | 10·0 | 7·01 |
| | 15·0 | 8·43 |
| | 20·0 | 9·61 |
| | 25·0 | 10·55 |
| 0·0452 | 10·0 | 4·5 |
| | 20·0 | 7·3 |
| | 30·0 | 8·9 |
| 0·1130 | 30·0 | 24·4 |
| | 33·5 | 30·2 |
| | 35·9 | 32·3 |
| | 40·0 | 33·3 |
| | 49·7 | 37·2 |
| | 80·0 | 48·2 |
| | 100·0 | 56·9 |

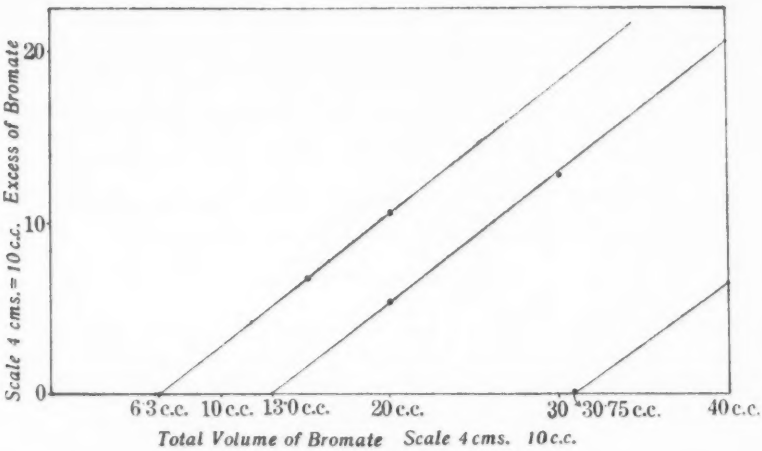
TABLE II

*Resacetophenone (gm.)*

| Taken | Found | Error (%) |
|---|---|---|
| 0·0226 | 0·0233 | 3·1 |
| 0·0452 | 0 0482 | 6·7 |
| 0·1130 | 0·1140 | 0·9 |

In evaluating the magnitude of the error, it should be noted that the graphical method involves a certain amount of approximation of the figures depending on the scale used. It is estimated, therefore, that the maximum error is of the order of 5%.

It is to be noted that the bromination is a slow and progressive reaction which goes beyond di- and tri-bromination stage. The solution becomes prematurely yellow with quantities of bromate even slightly less than the theoretical quantity required for di-bromination. At this stage the solution liberates iodine from potassium iodide indicating the presence of free bromine. It is therefore not possible to secure accurate values even for di-bromination by adding a slight excess of bromate and brominating for 10-15 minutes. The extrapolation method alone yields satisfactory results.




On brominating with a large excess, it was found that a fourth bromine atom entered the molecule by replacing either one of the hydroxyls or the nuclear acetyl group. By analogy with the behaviour of saligenin, salicylic acid and aldehyde it may be inferred that it is the nuclear acetyl and not the phenolic group that is replaced. During later stages of bromination the insoluble bromo compound goes into solution.

## SUMMARY

Quantitative studies on the bromination of resacetophenone showed that the reaction was slow and progressive and its magnitude depended primarily on the amount of bromate initially added in excess of the theoretical equivalent so that reproducible results could not be obtained directly by Koppeschaar's method. However, on plotting the volume of bromate initially added against the excess found by titration, a linear graph was obtained which on extrapolation to zero excess gave the value of bromate equivalent to di-bromination of the ketone present in solution. The estimated maximum error involved was of the order of 5%.

## REFERENCES

1. Mayer .. *Nachweis and Bestimmung Organischer Verbindungen*, 1933, **2**, 231.
2. Koppeschaar .. *Zeit. anal. Chem.*, 1876, **15**, 234.
3. Rudermann .. *Ind. Eng. Chem. Anal. Ed.*, 1946, 753.

# INSECTICIDAL PROPERTIES AND CHEMICAL CONSTITUTION

## Part VI. Some Phenyl and Halogen substituted Coumarins

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In previous parts of this series[1-5] were presented results relating to the activity of pyrones and related compounds as fish poisons. Among them the coumarins are the easiest to prepare. A side phenyl nucleus in the 3- or 4-position of the coumarin molecule is essential for high toxicity.[2] It was also noticed that a hydroxyl group in the 5-position was more favourable than one in the 7-position.[2] In continuation, a few new compounds (coumarins) have been prepared embodying these features. 5-Hydroxy- and 5-methoxy-3-phenyl-4-methyl coumarins and 5-hydroxy- and 5-methoxy-4-phenyl coumarins have been synthesised. In order to test the influence of the presence of more phenyl groups, 3:4-diphenyl derivatives have also been prepared.

The presence of halogen atoms has been recognised as useful for the enhancement of toxic properties. In the preparation of compounds containing them, the influence of the position occupied by these atoms has to be taken into account. The preparation of the required chloro and bromo coumarins has already been described elsewhere.[6-8] A careful investigation of the toxicity of bromo-compounds was first carried out in order to understand the influence of halogen atoms and based on this knowledge, select cases of chloro-derivatives have also been examined.

Originally *Haplochilus panchax*, a small fresh water fish, which is available on the eastern coast of India, was employed. But this is not found in Delhi and it was not easy to transport large numbers of the original fish and keep them at Delhi for experimental purposes. Hence a small fresh-water fish, commonly available in Delhi, has been used. This has been identified as *Barbus tetrarupegus*. In order to make comparisons with older data, it was necessary to carry out tests with some of the older compounds using the new fish. It was noticed that *Barbus tetrarupegus* is considerably more sensitive and therefore smaller quantities of substances could be used for the tests.

The preparation of new compounds used for the tests and not reported elsewhere is given in the experimental part. The results of toxicity experiments are presented in Tables I and II.

The introduction of a methyl or a phenyl group in the 4-position does not seem to enhance the toxic properties of 3-phenyl umbelliferone. However if the molecular weights are taken into consideration, mole for mole, 3:4-diphenyl-7-hydroxy coumarin is better than 3-phenyl umbelliferone. As expected, 5-hydroxy-3-phenyl-4-methyl coumarin is considerably more toxic than the isomeric 7-hydroxy compound. Similarly 5-hydroxy-4-phenyl coumarin exhibits high toxicity. The earlier observation[1–5] that the methyl ethers are more toxic than the corresponding hydroxy compounds is confirmed in these experiments.

Among the bromo compounds it can be readily seen that the 3-bromo derivative of 4-methyl umbelliferone is far superior to the nuclear brominated (6-) derivative. However in conjunction with a bromine atom in the 3-position, bromine atoms in the 6- and 8-positions enhance the toxic properties considerably (3:6- and 3:8-dibromo derivatives). 3:6:8-Tribromo-4-methyl umbelliferone is however far less toxic than either 3:6- or 3:8-dibromo compounds. Solubility considerations also play an important part. Whereas the 3-substituted compound is quite easily soluble, the nuclear brominated derivatives of courmains (6- and 8- bromo umbelliferones) are far less soluble. Among the dibromo-compounds, those having bromine atoms in the 3-position are comparatively more soluble.

TABLE I

*Past results with* Haplochilus panchax (*for comparison*)[2]

| No. | Substance | Conc. mgm. per litre | Turning time min. | Mol. wt. of substance | Remarks |
|---|---|---|---|---|---|
| 1 | 4-Methyl-7-hydroxy coumarin .. | 200<br>150 | 34·5<br>58·0 | 176 | |
| 2 | 4-Methyl-7-methoxy coumarin .. | 100<br>67<br>50 | 6·0<br>11·0<br>25·5 | 190 | |
| 3 | 3-Phenyl-7-hydroxy coumarin .. | 100<br>30<br>20 | 3·5<br>15·0<br>29·0 | 238 | |
| 4 | 3-Phenyl-7-methoxy coumarin .. | 10<br>5 | 9·0<br>28·5 | 252 | |

TABLE II

*New Results with* Barbus tetrarupegus

| No. | Substance | Conc. mgm. per litre | Turning time min. | Mol. Wt. of substance | Remarks |
|---|---|---|---|---|---|
| 1 | 3-Phenyl-7-hydroxy coumarin | 30 | 3·2 | 238 | |
| | | 20 | 5·9 | | |
| 2 | 3-Phenyl-7-methoxy coumarin .. | 5 | 10·0 | 252 | |
| 3 | 3-Phenyl-4-methyl-7-hydroxy coumarin[6] .. | 20 | 7·5 | 252 | |
| 4 | 3-Phenyl-4-methyl-7-methoxy coumarin[6] .. | 20 | 0·8 | 266 | |
| | | 10 | 3·8 | | |
| | | 5 | 8·6 | | |
| 5 | 3:4-Diphenyl-7-hydroxy coumarin .. | 20 | 7·6 | 314 | |
| 6 | 3:4-Diphenyl-7-methoxy coumarin .. | 10 | 18·6 | 328 | |
| 7 | 3-Phenyl-4-methyl-5-hydroxy coumarin .. | 20 | 2·4 | 252 | |
| | | 10 | 5·7 | | |
| 8 | 3-Phenyl-4-methyl-5-methoxy coumarin .. | 5 | 9·0 | 266 | |
| 9 | 4-Phenyl-5- hydroxy-coumarin .. | 20 | 2·4 | 238 | |
| | | 10 | 6·3 | | |
| 10 | 4-Phenyl-5-methoxy coumarin .. | 5 | 5·9 | 252 | |
| 11 | 3-Chloro-4-methyl-7-hydroxy coumarin[9] .. | 80 | 4·4 | 210·5 | Fish tried to jump out at the beginning. All the fish died within 5·5 min. after turning |
| | | 40 | 10·0 | | All the fish died immediately after turning |
| 12 | 3-Chloro-4-methyl-7-methoxy coumarin[7] .. | 20 | 4·8 | 224·5 | |
| 13 | 3-Chloro-4:7-dimethyl-5-hydroxy coumarin[9] | 20 | 57·0 | 224·5 | |
| 14 | 3-Bromo-4-methyl-7-hydroxy coumarin[10] .. | 80 | 4·2 | 255 | One fish died immediately |
| | | 40 | 9·5 | | All fish died immediately |
| 15 | 3-Bromo-4-methyl-7-methoxy coumarin [11] .. | 20 | 6·4 | 269 | |
| 16 | 4-Bromomethyl-7-hydroxy coumarin[6] .. | 80 | 27·3 | 255 | |
| 17 | 6-Bromo-4-methyl-7-hydroxy coumarin[12, 13] | 40 | .. | 255 | No effect in 15 hours |
| 18 | 6-Bromo-4-methyl-7-methoxy coumarin[13] .. | 13 | .. | 269 | No effect in 2 hours |
| 19 | 3:6-Dibromo-4-methyl-7-hydroxy coumarin[10] | 40 | 4·0 | 334 | One fish died |
| 20 | 3:8-Dibromo-4-methyl-7-hydroxy coumarin[10] | 40 | 3·0 | 334 | The fish jumped violently |
| 21 | 3:6:8-Tribromo-4-methyl-7-hydroxy coumarin[10] .. | 40 | 18·0 | 413 | |
| 22 | 3-Bromo-4-phenyl-7-hydroxy coumarin[8] .. | 20 | 9·6 | 317 | Fish very much affected. Recovered only very slowly |
| | | 10 | 19·5 | | Two fish died |
| 23 | 3-Bromo-4-phenyl-7-methoxy coumarin[8] .. | 10 | 5·9 | 331 | The fish were very restless and were affected seriously |
| 24 | 3-Chloro-4-phenyl-7-methoxy coumarin[8] .. | 10 | 5·3 | 286·5 | |
| 25 | 6-Bromo-3 phenyl-7-hydroxy coumarin[6] .. | 20 | 5·8 | 317 | |
| 26 | 8-Bromo-3-phenyl-7-hydroxy coumarin[6] .. | 20 | 7·1 | 317 | Fish tried to jump out |
| 27 | 6:8-Dibromo-3-phenyl-7-hydroxy coumarin[6] | 20 | 9·4 | 396 | All the fish died immediately after turning |
| 28 | 6:8-Dibromo-3-phenyl-4-methyl-7-hydroxy coumarin[6] | 20 | .. | 410 | No effect in 25 min. |

The bromo derivatives of 3-phenyl umbelliferone are not more useful than the unsubstituted coumarin itself. Here again comparison of molar quantities would lead to the conclusion that bromination in this series also

enhances toxic properties slightly. The bromo derivatives of 3-phenyl-4-methyl umbelliferone and the methyl ethers of brominated 3-phenyl umbelliferones[6] could not be tested owing to their low solubilities. Although 6:8-dibromo-3-phenyl umbelliferone is not as toxic as 3-phenyl umbelliferone, it has a greater lethal effect since all the fish employed in the experiment using it died immediately after turning.

Bromo and chloro derivatives have nearly the same toxicity and therefore substitution of chlorine atoms in place of bromine atoms does not have a marked effect. Considering molar proportions, bromo-compounds may be said to be the better of the two. But chloro-compounds should be eventually cheaper to prepare and they seem to be more soluble.

One negative substituent, a phenyl group in either the 3- or the 4-position or a halogen atom in the 3-position increases toxicity considerably, the effect of the former being far more prominent. But the effect of further substitution in these positions is not additive. 3:4-Diphenyl umbelliferone and 3-bromo-4-phenyl umbelliferone and their methyl ethers and 3-chloro-4-phenyl-7-methoxy coumarin are less toxic than the related monophenyl umbelliferones and their methyl ethers. This is in agreement with an earlier observation in the case of chromones,[4] where it was found that 7-hydroxy-2:3-diphenyl chromone was much less toxic than 7-hydroxy-2-phenyl or 7-hydroxy-3-phenyl chromone.

3-Chloro-4:7-dimethyl-5-hydroxy coumarin seems to have an unexpectedly low toxicity, taking into consideration the high toxicity exhibited in general by 5-hydroxy coumarins. This could possibly be explained as due to the presence of a methyl group in the 7-position which could exert an effect somewhat similar to an hydroxyl group. If such is the case, the result is not unusual since 5:7-dihydroxy-4-methyl coumarin in which both the 5- and 7-positions are occupied is much inferior to either 5- or 7-hydroxy-4-methyl coumarin.[2]

## EXPERIMENTAL

### 3:4-*Diphenyl-7-acetoxy coumarin*

Resbenzophenone[15] (4 g.), sodium phenyl acetate (8 g.) and acetic anhydride (50 c.c.) were heated together at 170–80° for four hours and the mixture poured into crushed ice. An yellow semi-solid mass separated out on leaving overnight. The aqueous layer was decanted off and the semi-solid washed first with water and then with petroleum ether by decantation. The residual petroleum ether was removed on a water bath. On adding alcohol to the residue, a colourless solid separated out. It was filtered and

washed with cold alcohol. Yield 6 g. On crystallisation from alcohol, 3 : 4-diphenyl-7-acetoxy coumarin was obtained as colourless rectangular prisms melting at 222–23°. (Found: C, 77·3; H, 4·6; $C_{23}H_{16}O_4$ requires C, 77·5; H, 4·5%.) Bargellini[14] carried out this reaction for 30 hours and obtained a poor yield of the acetate, which he describes as yellowish crystals, m.p. 220°.

3 : 4-*Diphenyl-7-hydroxy coumarin*

The above acetate (4 g.) was dissolved in aqueous alcohol (1 : 2; 200 c.c.) and concentrated sulphuric acid (10 c.c.) was added and the solution refluxed for 2 hours. On cooling, the 7-hydroxy compound separated. Yield 3 g. It was crystallised twice from alcohol. It was obtained in the form of stout colourless prisms melting at 286–87°. Further crystallisations did not raise the m.p. It was sparingly soluble in alcohol. Bargellini[14] gives the m.p. as 290° (Found: C, 80·0; H, 4·4; $C_{21}H_{14}O_3$ requires C, 80·3; H, 4·5%).

3 : 4-*Diphenyl-7-methoxy coumarin*

3 : 4-Diphenyl-7-hydroxy coumarin (2·8 g.) was dissolved in dry acetone (200 c.c.) and dimethyl sulphate (0·93 c.c.) and anhydrous potassium carbonate (5 g.) were added and the mixture gently refluxed for 6 hours. The acetone solution was filtered off and the potassium salts were washed with warm acetone. The solvent was distilled off and the residue treated with water to decompose excess of dimethyl sulphate. The solid was filtered and when dry, crystallised from benzene. It separated as colourless rectangular rods, m.p. 175–77°. Yield 2·5 g. (Found: C, 80·4; H, 4·8; $C_{22}H_{16}O_3$ requires C, 80·5; H, 4·9%).

3-*Phenyl-4-methyl-5-hydroxy coumarin*

A mixture of 2 : 6-dihydroxy acetophenone[16] (4 g.), fused sodium phenyl acetate (8 g.) and acetic anhydride (50 c.c.) was heated at 170–80° for 4 hours. The product was crystallised twice from alcohol when it separated as colourless stout rectangular rods melting at 150–52°. Yield 5·5 g. This acetate (5 g.) was hydrolysed with 10% alcoholic sulphuric acid (150 c.c.) by refluxing on a water-bath for one hour. The solution was diluted with water (100 c.c.) and the alcohol was distilled off. The mixture was cooled and the precipitate of 5-hydroxy-3-phenyl-4-methyl coumarin filtered off. Yield 4 g. It was crystallised twice from alcohol. Colourless rectangular prisms, m.p. 276–78°. It did not give any colour with alcoholic ferric chloride and dissolved easily in dilute aqueous sodium hydroxide and dilute aqueous sodium carbonate to give yellow solutions. These reactions show that the product is a 5-hydroxy coumarin and not a 5-hydroxy chromone (Found: C, 76·5; H, 5·2; $C_{11}H_{16}O_3$ requires C, 76·2; H, 4·8%).

*3-Phenyl-4-methyl-5-methoxy coumarin*

The above hydroxy coumarin (1·32 g.) was methylated with dimethyl sulphate (0·6 c.c.) and anhydrous potassium carbonate (3 g.) in dry acetone solution. 3-Phenyl-4-methyl-5-methoxy coumarin (1 g.) was crystallised twice from alcohol. It separated as colourless prisms tapering at both ends. m.p. 165–66° (Found: C, 77·1; H. 5·2; $C_{17}H_{14}O_3$ requires C, 76·7; H, 5·3%).

*4-Phenyl-5-acetoxy coumarin*

A mixture of 2 : 6-dihydroxy benzophenone[17] (4 g.), fused sodium acetate (10 g.) and acetic anhydride (50 c.c.) was refluxed on an oil bath at 170–80° for 24 hours, cooled and poured into crushed ice. A heavy viscous brown oil separated on leaving overnight. It was separated from the aqueous portion by decantation, was washed first with water and then thrice with petroleum ether. The traces of petroleum ether remaining were removed by heating on a water bath. Treatment of the residual oil with cold alcohol (10 c.c.) yielded a colourless solid, which was filtered and washed with alcohol. Yield 1·7 g. It crystallised from alcohol as colourless stout prisms melting at 170–71° (Found: C, 72·8; H, 4·4; $C_{17}H_{12}O_4$ requires C, 72·9; H, 4·3%).

*4-Phenyl-5-hydroxy coumarin*

4-Phenyl-5-acetoxy coumarin (3 g.) was refluxed with 10% alcoholic sulphuric acid (150 c.c.) for a period of two hours. The solution was diluted with water (100 c.c.) and as much of the alcohol as possible was distilled off on a water-bath. On cooling, the hydroxy coumarin separated out. Yield 2·5 g. It crystallised from alcohol as very stout prismatic crystals melting at 221–22°. It did not give any colour with ferric chloride in alcoholic solution and was soluble in aqueous sodium carbonate to give a yellow solution (Found: C, 75·2; H, 4·2; $C_{15}H_{10}O_3$ requires C, 75·6; H, 4·2%).

*4-Phenyl-5-methoxy coumarin*

4-Phenyl-5-hydroxy coumarin (0·7 g.) was methylated in dry acetone solution with dimethyl sulphate (0·35 c.c.) and excess of potassium carbonate. 5-Methoxy-4-phenyl coumarin crystallised from alcohol as stout rectangular prisms melting at 98–100° (Found: C, 76·1; H, 4·5; $C_{16}H_{12}O_3$ requires C, 76·2; H, 4·8%).

## SUMMARY

A number of phenyl and halogen substituted coumarins with substituents in different positions have been examined as fish poisons. The presence of a phenyl group in the 3 or 4 position or a halogen atom in the

3-position seems to be most favourable. Higher substitution does not appreciably enhance the toxic properties. In consonance with previous results, a hydroxyl group in the 5-position seems to produce greater toxicity than one in the 7-position.

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## References

1. Murti, Rao and Seshadri .. *Proc. Ind. Acad. Sci.*, 1947, **25 A**, 22.
2. ——— and Seshadri .. *Ibid.*, 1947, **25 A**, 333.
3. Seshadri and Viswanadam .. *Ibid.*, 1947, **25 A**, 337.
4. Murti, Row and Seshadri .. *Ibid.*, 1948, **27 A**, 33.
5. Narasimhachari and Seshadri .. *Ibid.*, 1948, **27 A**, 128.
6. Seshadri and Varadarajan .. *J. S. I. R.*, 1952, **11 B**, 39.
7. Grover, Seshadri and Varadarajan .. *Ibid.*, 1952, **11 B**, 50,
8. Seshadri, Subramani and Varadarajan *Ibid.*, 1952, **11 B**, 56.
9. Pechmann and Hancke .. *Ber.*, 1901, **34**, 357.
10. Sethna and Dalvi .. *J. I. C. S.*, 1949, **26**, 360.
11. Limaye and Bhide .. *Rasayanam*, 1938, **1**, 38.
12. Fries and Lindemann .. *Ann.*, 1914, **404**, 53.
13. Chakravarti and Mukerjee .. *J. I. C. S.*, 1937, **14**, 728.
14. Bargellini .. *Chem. Abs.*, 1926, 595.
15. Komarowski and Kostanecki .. *Ber.*, 1894, **27**, 1997.
16. Limaye .. *Ibid.*, 1932, **65**, 375.
17. ——————— .. *Ibid.*, 1934, **67**, 12.

# NUCLEAR OXIDATION IN FLAVONES AND RELATED COMPOUNDS

## Part XXXVII. Isomerisation of 2:3-dimethyl-5:7:8-trihydroxy chromone

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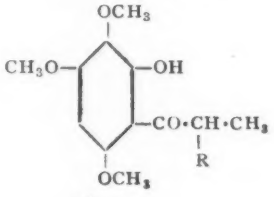
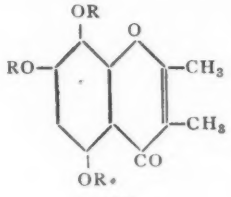
In earlier publications[1–4] dealing with the members of the flavone, chromone and isoflavone series, it has been established that when the 3-position is unsubstituted, isomeric change from the 5:7:8-trihydroxy type into the 5:6:7-trihydroxy type takes place on boiling with hydriodic acid. But if a methoxyl (hydroxyl) or a phenyl group should be present in this position, the isomeric change is prevented.[3–5] Substitution in the 2-position does not seem to have any effect. In order to get information as to whether a free hydrogen in the 3-position is essential in this isomeric change and any kind of substitution will prevent it, experiments have now been carried out with chromones having a methyl group in this position. The simplest example will be 2:3-dimethyl-5:7:8-trimethoxy chromone (II *b*). This has now been prepared from 2-hydroxy-3:4:6-trimethoxy propiophenone (I *a*)[6] by conversion into its α-acetyl derivative (I *b*) and subsequent chromone ring closure. Demethylation of this substance (II *b*) with aluminium chloride in benzene solution yields a trihydroxy compound having all the properties expected for the 5:7:8-trihydroxy arrangement (II *a*). This reagent is known not to produce any rearrangement (see for example wogonin dimethyl ether[1].)




(I)

*a*, R = H

*b*, R = $COCH_3$



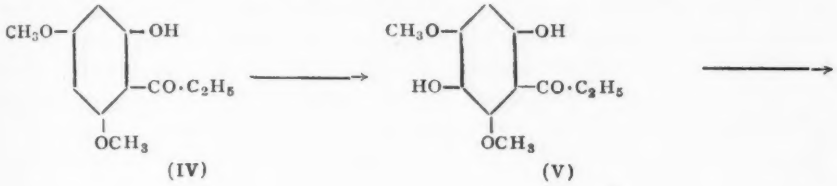

(II)

*a*, R = H

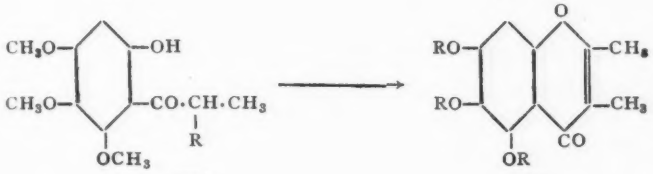
*b*, R = $CH_3$

On the other hand, hydriodic acid yields a different product giving different reactions. It should therefore be 2:3-dimethyl-5:6:7-trihydroxy

chromone (III *a*). On methylation, it gives rise to a trimethyl ether (III *b*) different from the original 2 : 3-dimethyl-5 : 7 : 8-trimethoxy chromone (II *b*). Thus, even though the 3-position is substituted by a methyl group, the isomeric change has occurred and hence it could be concluded that the presence of a hydrogen atom in this position is not essential for this purpose and that the nature of the substituent is also important.



(IV) (V)



(VI) (III)

*a*, R=H *a*, R=H

*b*, R=$COCH_3$ *b*, R=$CH_3$

For purposes of comparison, an authentic sample of 2 : 3-dimethyl-5 : 6 : 7-trimethoxy chromone (III *b*) has now been prepared starting from 2-hydroxy-4 : 6-dimethoxy propiophenone (IV). It is first subjected to nuclear oxidation by alkaline persulphate to yield 2 : 5-dihydroxy-4 : 6-dimethoxy propiophenone (V), which is partially methylated to (VI *a*) and employed for chromone ring closure through the diketone (VI *b*) as intermediate according to the procedure described above for the synthesis of the isomeric trimethoxy chromone (II *b*).

## Experimental

*2-Hydroxy-3 : 4 : 6-trimethoxy propiophenone* (I *a*)

This was prepared earlier by Bargellini[6] by the interaction of 1 : 2 : 3 : 5-tetramethoxy benzene and propionyl chloride in presence of aluminium chloride in carbon disulphide solution. The reaction has now been more conveniently carried out in ether solution.

Tetramethoxy benzene (11 g.) was added to a solution of anhydrous aluminium chloride (11 g.) in dry ether (100 c.c.) cooled to 0°. Propionyl chloride (6·5 c.c.) was then added to the cooled mixture with vigorous

stirring during the course of one hour and the mixture was set aside for 24 hours. The yellow aluminium chloride complex that had separated was decomposed by the cautious addition of concentrated hydrochloric acid (15 c.c.) and pieces of ice. The mixture was then heated on a water-bath for half an hour, the ether being allowed to distil away. The hot mixture was extracted with benzene (150 c.c.) and the benzene extract washed twice with dilute hydrochloric acid and then once with water. It was then extracted exhaustively with aqueous sodium hydroxide (10%). On acidification of the combined alkaline extract, 2-hydroxy-3 : 4 : 6-trimethoxy acetophenone separated as a light yellow powder. It was filtered, washed with water and crystallised from alcohol, when it came out as long thick fawn coloured rectangular prisms melting at 129–30°. Yield 7·5 g. Bargellini[6] reported the m.p. as 124–26°.

*2-Hydroxy-3 : 4 : 6-trimethoxy-α-acetyl propiophenone (I b)*

A solution of 2-hydroxy-3 : 4 : 6-trimethoxy propiophenone (2 g.) in dry ethyl acetate (20 c.c.) was added to powdered sodium (2 g.) just covered with a layer of dry ether. When the initial reaction was over, the mixture was heated under reflux on a water-bath. The yellow sodium salt of the diketone began to separate after about twenty minutes. After one hour, more ethyl acetate (10 c.c.) was added and the refluxing continued for 4 hours. The yellow sodium salts were dissolved in ice cold water; the aqueous solution was separated from unreacted ethyl acetate and acidified with glacial acetic acid. The diketone separated as pale yellow crystals on leaving overnight in the refrigerator. These were collected and washed with a small quantity of ether. It crystallised from a mixture of chloroform and petroleum ether as colourless rectangular prisms with tapering edges and melted at 133–34°. Yield 1·45 g. With ferric chloride in alcoholic solution, it gave a pale greenish brown colour (Found: C, 59·9; H, 6·2; $C_{14}H_{18}O_6$ requires C, 59·6; H, 6·4%).

*2 : 3-Dimethyl-5 : 7 : 8-trimethoxy chromone (II b)*

The above diketone (1·3 g.) was dissolved in rectified spirits (15 c.c.), concentrated sulphuric acid (4 drops) added and the solution refluxed on a water-bath for 15 minutes. It was then cooled and diluted with water and the precipitated crystalline mass was recrystallised from dilute alcohol. 2 : 3-Dimethyl-5 : 7 : 8-trimethoxy chromone came out as colourless silky needles melting at 160–61°. Yield 1 g. It did not give any colour with ferric chloride (Found: C, 63·8; H, 6·3; $C_{14}H_{16}O_5$ requires C, 63·6; H, 6·1%).

2: 3-*Dimethyl*-5: 7: 8-*trihydroxy chromone* (*II a*)

To a solution of 2: 3-dimethyl-5: 7: 8-trimethoxy chromone (0·95 g.) in dry benzene (15 c.c.), was added anhydrous aluminium chloride (2 g.) and the mixture was heated under reflux for two hours. The solvent was then distilled off and the residual aluminium chloride complex was cooled and decomposed by cautiously adding pieces of ice and concentrated hydrochloric acid (6 c.c.). The resulting yellow powder was filtered, washed with a little ether and crystallised from a mixture of ethyl acetate and alcohol when the trihydroxy-dimethyl chromone separated as thick yellow rhombic prisms melting at 243–44°. Yield 0·7 g. With ferric chloride in alcoholic solution, it gave a deep green colour which changed to brown with excess of the reagent. It dissolved in aqueous sodium carbonate (5%) to give a deep pink solution which changed quickly to yellow and then faded (Found: C, 59·1; H, 4·4; $C_{11}H_{10}O_5$ requires C, 59·5; H, 4·5%).

2-*Hydroxy*-4: 6-*dimethoxy propiophenone* (*IV*)

This was prepared earlier by Canter, Curd and Robertson[7] by the Hoesch reaction using phloroglucinol dimethyl ether and propio-nitrile. For the present work the Friedel Crafts reaction was carried out as given below.

To a solution of anhydrous aluminium chloride (68 g.) in dry ether (300 c.c.) cooled to 0°, was added with stirring, phloroglucinol trimethyl ether[8] (34 g.), followed by propionyl chloride (23 c.c.) during one and a half hours, the temperature being maintained at 0°. After 48 hours, the aluminium chloride complex was decomposed with the addition of pieces of ice and concentrated hydrochloric acid (70 c.c.). The ether was then distilled off and the hot aqueous solution extracted with benzene. Extraction of the benzene solution with aqueous alkali and subsequent acidification gave the hydroxy dimethoxy ketone. It crystallised from alcohol as colourless elongated plates melting at 111°. Yield 30 g. Canter *et al.*[7] give same m.p. It gave a blue colour with nitric acid.

The benzene solution left after extraction with alkali was washed with water and evaporated. The residue crystallised from alcohol as pale yellow long thick rectangular rods melting at 136–37°. It was evidently 2: 4: 6-trimethoxy propiophenone. It did not give any colour with alcoholic ferric chloride (Found: C, 64·7; H, 7·3; $C_{12}H_{16}O_4$ requires C, 64·3; H, 7·1%).

2: 5-*Dihydroxy*-4: 6-*dimethoxy propiophenone* (*V*)

2-Hydroxy-4: 6-dimethoxy propiophenone (12 g.) was dissolved in aqueous sodium hydroxide (11 g. in 80 c.c. of water) and to this stirred

solution, maintained at 15–17°, was added dropwise a solution of potassium persulphate (19 g.) in water (350 c.c.) in the course of 5 hours. It was set aside and after 36 hours acidified to congo red with concentrated hydrochloric acid. The precipitated solid (2 g.) consisting of the unreacted material was filtered off and the filtrate extracted twice with ether. Norit (6 g.) and sodium bisulphite (5 g.) were then added, the mixture stirred well and filtered. The residual charcoal was washed with water. The filtrate was heated on a boiling water-bath to remove dissolved ether and to the hot solution was added concentrated hydrochloric acid (150 c.c.) with stirring. On allowing the clear deep red solution to cool, bright shining crystals of the dihydroxy compound separated. A further quantity came out on cooling the mixture to 0°. These crystals were filtered off. Some more of the substance was obtained by ether extraction of the aqueous mother liquors. When crystallised from alcohol twice, it came out as bright yellow irregular prisms melting at 120–21°. Yield 4·0 g. With ferric chloride in alcoholic solution, it gave a transient green colour which quickly faded. Addition of more of the reagent gave a permanent orange red solution. It dissolved in aqueous sodium hydroxide to give a bright yellow solution which fades slowly in the cold, but quickly on heating. It gave a red colour with concentrated nitric acid and with concentrated sulphuric acid produced a yellow colour changing to orange and then to violet brown on warming (Found: C, 58·4; H, 5·8; $C_{11}H_{14}O_5$ requires C, 58·4; H, 6·2%).

Sastri and Seshadri[9] recorded that with alcoholic ferric chloride, 2:5-dihydroxy-4:6-dimethoxy acetophenone gives a transient green colour changing to brown and its solution in aqueous sodium hydroxide is yellow at first and then changes to reddish brown. A pure sample of this ketone is now found to exhibit the same colour reactions as recorded for 2:5-dihydroxy-4:6-dimethoxy propiophenone above.

*2-Hydroxy-4:5:6-trimethoxy propiophenone* (*VI a*)

A solution of 2:5-dihydroxy-4:6-dimethoxy propiophenone (3·75 g.) in dry benzene (200 c.c.) was mixed with dimethyl sulphate (1·9 c.c.) and anhydrous potassium carbonate (5 g.) and the mixture refluxed for 12 hours. Water (100 c.c.) was then added to the hot mixture. The potassium salts dissolved on vigorous shaking. The aqueous layer was drawn off and the benzene solution extracted with aqueous sodium carbonate (10%). It was then extracted with aqueous sodium hydroxide (10%) repeatedly and the combined alkaline extract cooled to 0° and acidified. 2-Hydroxy-4:5:6-trimethoxy propiophenone was precipitated as an oil. It was extracted with ether and the ether extract dried over anhydrous sodium sulphate and

the solvent evaporated. The oil that was left did not solidify and hence was employed directly for the diketone condensation.

*2-Hydroxy-4 : 5 : 6-trimethoxy-α-acetyl propiophenone* (*VI b*)

2-Hydroxy-4 : 5 : 6-trimethoxy propiophenone (1·7 g.) was condensed with sodium (2 g.) and ethyl acetate (20 c.c.) in the same way as the isomeric 2-hydroxy-3 : 4 : 6-trimethoxy propiophenone (*I a*) described earlier. The diketone crystallised from ethyl acetate as colourless rectangular plates melting at 204–6°. Yield 0·5 g. It gave a deep bluish green colour with ferric chloride in alcoholic solution (Found: C, 59·7; H, 6·0; $C_{14}H_{18}O_6$ requires C, 59·6; H, 6·4%).

*2 : 3-Dimethyl-5 : 6 : 7-trimethoxy chromone* (*III b*)

To a solution of the above diketone (0·2 g.) in alcohol (5 c.c.), concentrated sulphuric acid (2 drops) was added and the mixture refluxed for 10 minutes. It was concentrated and diluted with water and allowed to cool. The trimethoxy chromone which separated was filtered and crystallised from very dilute alcohol. It was obtained as long narrow colourless rectangular plates melting at 135–135·5° (Found: C, 64·0; H, 6·4; $C_{14}H_{16}O_5$ requires C, 63·6; H, 6·1%).

*2 : 3-Dimethyl-5 : 6 : 7-trihydroxy chromone* (*III a*)

2 : 3-Dimethyl-5 : 7 : 8-trimethoxy chromone (*II b*) (1 g.) was dissolved in acetic anhydride (15 c.c.) and to the solution, cooled to 0°, hydriodic acid (20 c.c., d. 1·7) was added cautiously. The mixture was refluxed for 2 hours at 140° on an oil-bath. It was then cooled and diluted with aqueous sodium sulphite. The reddish brown powder that had seaparated after three hours was filtered, washed with water, dried and crystallised from a mixture of absolute alcohol and ethyl acetate. The trihydroxy chromone separated as long colourless needles and rectangular rods melting at 230–31°. Yield 0·7 g. It was sparingly soluble in ethyl acetate. With ferric chloride in alcoholic solution, it gave a deep bluish green colour which was unchanged on further addition of the reagent. It dissolved in aqueous sodium carbonate (5%) to give a pale green solution (Found in a sample dried at 110° in vacuuo: C, 59·5; H, 4·8; $C_{11}H_{10}O_5$ requires C, 59·5; H, 4·5%).

*Remethylation*

The above demethylated product (0·52 g.) was dissolved in dry acetone (50 c.c.) and treated with dimethyl sulphate (0·92 c.c., 4 moles) and potassium carbonate (4 g.). The mixture was refluxed on a water-bath for 8 hours. The solvent was then distilled off and water was added to the residue. The

resulting clear solution on standing for two days, deposited big crystals. These were filtered off and crystallised from very dilute alcohol. The methyl ether was obtained in the form of long narrow colourless rectangular plates melting at 135–135·5°, alone or when mixed with 2:3-dimethyl-5:6:7-trimethoxy chromone (III *b*) described earlier. Yield 0·4 g.

## SUMMARY

When boiled with hydriodic acid, 2:3-dimethyl-5:7:8-trimethoxy chromone undergoes besides demethylation, isomeric change also, yielding 2:3-dimethyl-5:6:7-trihydroxy chromone, thus showing that a free hydrogen atom in the 3-position is not essential for this isomeric change to take place and that the nature of the substituent is also important. For purposes of comparison, 2:3-dimethyl-5:7:8-trihydroxy chromone has been obtained by demethylation of the above trimethyl ether with aluminium chloride and 2:3-dimethyl-5:6:7-trimethoxy chromone by independent synthesis using nuclear oxidation as a stage.

## REFERENCES

1. Sastri and Seshadri .. *Proc. Ind. Acad. Sci.*, 1946, **24 A**, 243.
2. Rao, Seshadri and Viswanadam .. *Ibid.*, 1949, **29 A**, 72.
3. Chakravorty, Mukerjee, Murty and Seshadri *Ibid.*, 1952, **35 A**, 34.
4. Narasimhachari, Row and Seshadri *Ibid.*, 1952, **35 A**, 46.
5. Seshadri, Varadarajan and Venkateswarlu *Ibid.*, 1950, **32 A**, 250.
6. Bargellini .. *Gazetta*, 1915, **45** (i), 87.
7. Canter, Curd and Robertson .. *J. C. S.*, 1931, 1245.
8. Aghoramurty, Narasimhachari and Seshadri *Proc. Ind. Acad. Sci.*, 1951, **33 A**, 257.
9. Sastri and Seshadri .. *Ibid.*, 1946, **23 A**, 267.

# THE THERMO-OPTIC BEHAVIOUR OF QUARTZ

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## 1. Introduction

The refraction, dispersion and birefringence of quartz and their temperature variations have been the subject of numerous investigations. The literature on this subject prior to 1927 has been elaborately reviewed by Sosman[1] in his book on the properties of silica. Amongst the most significant of the earlier investigations was the work of Micheli[2] who showed that the temperature coefficients of the refractive indices which are negative in the visible region of the spectrum diminish in absolute magnitude with decreasing wave-length and after passing through a zero value actually change sign and become positive for the shortest ultra-violet wave-lengths. The work of Rinne and Kolb[3] is also of interest as they determined both the ordinary and extraordinary indices over a wide range of temperatures covering that at which the trigonal $\alpha$-form undergoes a reversible transformation to the hexagonal $\beta$-form. More recently also, Radhakrishnan[4] has determined by an interferometric method the temperature coefficients of the ordinary and the extraordinary indices of $\alpha$-quartz for temperatures between 0° C. and 400° C. Mention may also be made of the recent determinations by M. Barbaron[5] of the ordinary and the extraordinary indices of $\alpha$-quartz from — 200° C. to 50° C. for the wave-length 5460 Å.

The temperature variation of the refractive indices of quartz was explained in a general way by Pockels[6] and by Sosman.[7] As the volume of quartz increases with temperature, the refractive indices should decrease correspondingly. The actual changes are negative, as predicted, but numerically less. The true temperature effect, independent of the dilatation, must therefore be positive. This positive true temperature effect may be ascribed to the drift of the electronic dispersion wave-lengths towards longer wave-lengths. Using the Ketteler-Helmholtz formula and estimating the effect of temperature on the constants of the formula, Sosman has shown that the change in $\lambda_r$ the absorption wave-length comes out the same for

quartz and vitreous silica, the difference in the course of the indices in the two cases being entirely due to the difference in thermal expansions.

Radhakrishnan[8] has dealt with the thermo-optic behaviour of α-quartz on the basis of the general theory for crystals developed by Dr. G. N. Ramachandran. It is proposed in the present paper to discuss the thermo-optic behaviour of quartz over the entire range from −200° C. to 765° C. adopting a procedure different from that followed by Radhakrishnan.

## 2. General Discussion of the Data

As noted before, the course of the refractive indices with temperature depends upon the density changes and a positive part attributed to the drift of the spectral position of the dispersion frequencies. For a qualitative analysis of the data, we may base our discussion on the Gladstone-Dale formula connecting the indices with the density. S. Chandrasekhar[9] has shown that, when the close similarity in the spectroscopic behaviour of quartz and vitreous silica is considered and if one attempts to calculate the refraction of vitreous silica, the Gladstone-Dale formula gives the best results for refraction. Hence we may write

$$\left.\begin{aligned} n_{\omega 0} - 1 &= c_\omega \rho_0 \\ n_{\epsilon 0} - 1 &= c_\epsilon \rho_0 \end{aligned}\right\}, \tag{1}$$

at any initial temperature. Thus at any temperature $t$,

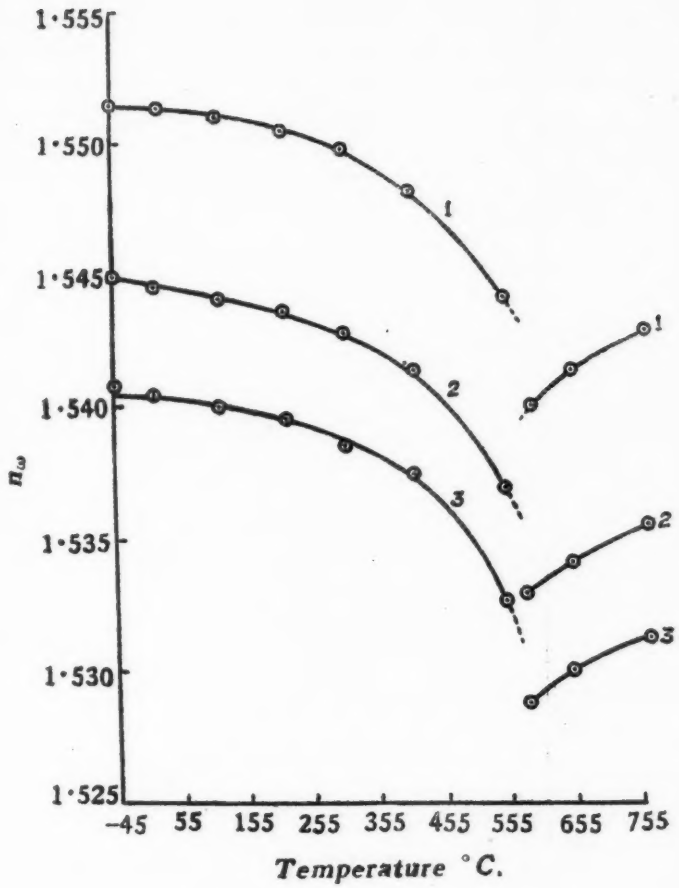
$$\begin{aligned} n_{\omega t} - 1 &= [n_{\omega 0} + \Delta n_\omega] - 1 \\ &= c_\omega \rho_0 + c_\omega \Delta\rho + \rho \Delta c_\omega. \\ &= c_\omega \rho_t + \mathrm{F}_\omega(t) \end{aligned}$$

where $\rho_t$ is the density at $t$, and $\mathrm{F}_\omega(t)$ is the positive contribution due to this temperature change, $c_\omega$ being considered approximately a constant. Thus we have at any temperature

$$\left.\begin{aligned} n_\omega - 1 &= c_\omega \rho + \mathrm{F}_\omega(t) \\ n_\epsilon - 1 &= c_\epsilon \rho + \mathrm{F}_\epsilon(t) \end{aligned}\right\} \tag{2}$$

where $c_\omega$ and $c_\epsilon$ are evaluated at any initial temperature.

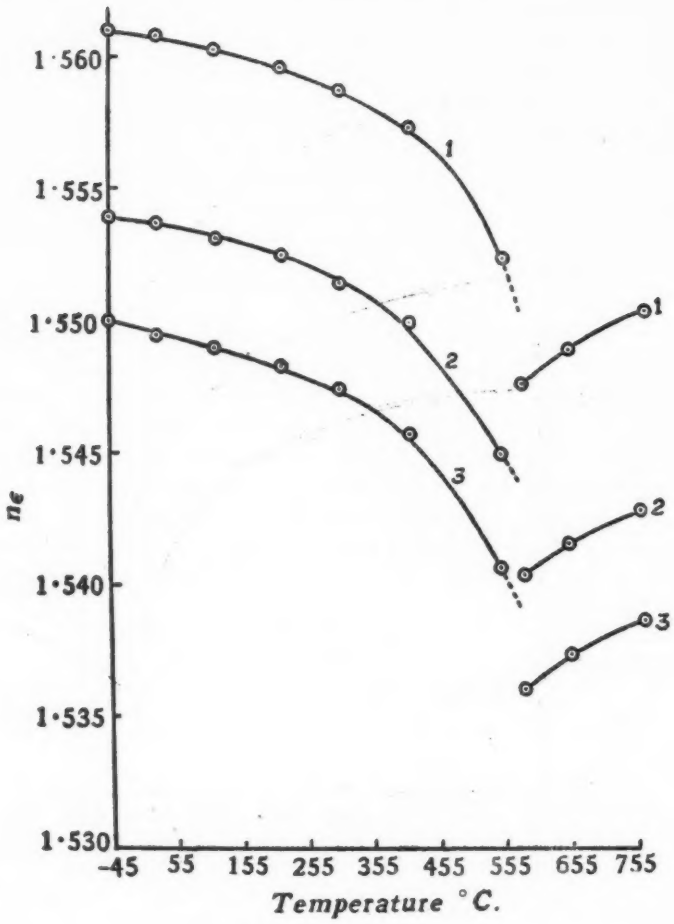
Figs. 1 and 2 showing the refractive indices at different temperatures for three typical wave-lengths have been plotted from Rinne and Kolb's data. As the temperature increases, the refractive indices fall off more and more rapidly as 573° C. is approached. At 573° C. the indices show a sudden drop. On further heating the refractive indices increase with temperature. This increase of the refractive indices beyond 573° C., *i.e.*, in β-quartz cannot




1 → 466·8 mμ
2 → 588·99 „
3 → 718·9 „

FIG. 1. Variation of ordinary refractive index with temperature

be fully explained by the small or negligible negative coefficient of thermal expansion, thus clearly showing that there is a positive part in the temperature variation of the refractive indices. In the region preceding 573° C., *i.e.*, in α-quartz, the refractive indices drop very much because of the enormous thermal expansion which is increasingly accelerated as the transition point is approached.

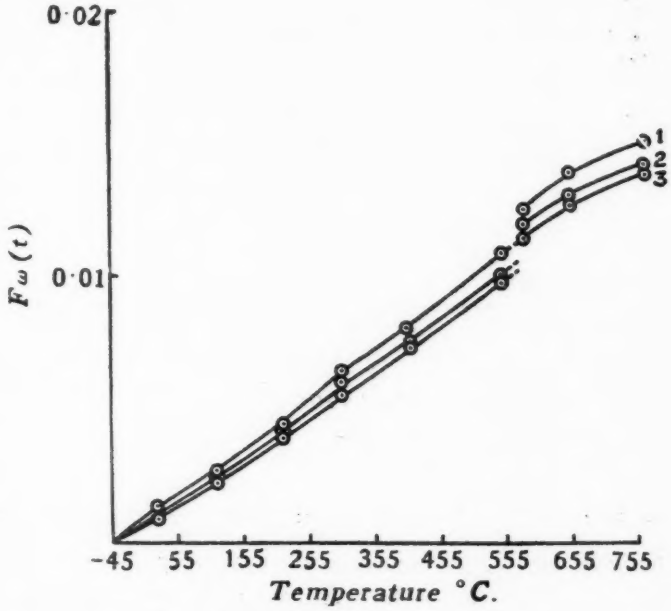



1 → 466·8 $m\mu$
2 → 588·99 ,,
3 → 718·9 ,,

FIG. 2. Variation of extraordinary refractive index with temperature

Figs. 3 and 4 show $F_\omega(t)$ and $F_\epsilon(t)$ at various temperatures. The $c_\omega$'s and $c_\epsilon$'s are calculated from the data for −45° C. We see from Figs. 3 and 4 that both in α-quartz and β-quartz, there is a positive part in the temperature variation of the refractive indices and this shows a steady increase. This part is completely submerged by the predominant negative effect in

the range preceding 573° as can be seen on comparing Figs. 1 and 3. We also see in Figs. 3 and 4 that there is a sudden increase in $F(t)$ at the transition temperature, while in Figs. 1 and 2 there is a sudden drop in the refractive indices. This means that the abrupt diminution in the refractive indices at the transition temperature is not wholly explicable in terms of the abrupt change of density. The structural changes represented by the $\alpha$-$\beta$ transformation cause a change in the opposite direction, *i.e.*, an increase in the refractive indices.




$n_\omega - 1 = c_\omega \rho + F_\omega(t)$

1 → 466·8 $m\mu$

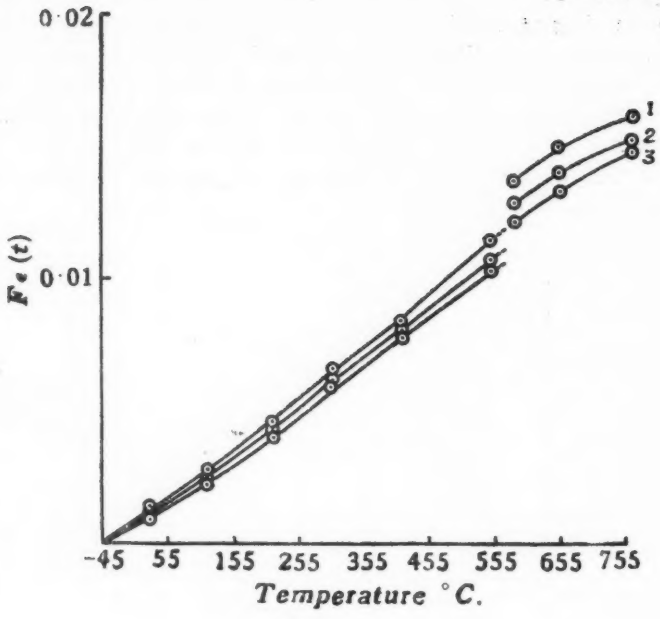
2 → 588·99 ,,

3 → 718·9 ,,

FIG. 3. Positive part in the temperature variation of ordinary index

## 3. DISPERSION FREQUENCIES OF QUARTZ

A variety of dispersion formulæ have been proposed for quartz. Our knowledge of the ultra-violet absorption spectrum of quartz is very meagre. Quartz even in the thinnest layers, is opaque to ultra-violet beyond about 1,400 Å. Tousey has observed two reflection maxima at 1,060 Å and 1,190 Å. If a dispersion formula using 1,060 Å and 1,190 Å is devised, a




$n_e - t = c_e\rho + F_e(t)$

1 → 466·8 $m\mu$

2 → 588·99 ,,

3 → 718·9 ,,

FIG. 4. Positive part in the temperature variation of extraordinary index

very substantial part of the refraction has to be attributed to a hypothetical absorption wave-length below 1,000 Å. Indeed it is quite possible to devise a number of different formulæ, using different absorption wave-lengths with suitable weights, all of which represent the refractive indices within known limits of accuracy. Thus it is not possible to fix uniquely the ultra-violet absorption wave-lengths from the refractive index data, and an element of arbitrariness therefore arises in devising such formulæ. However, if we limit ourselves to a particular part of the spectrum, say the visible spectrum, it is found in the case of quartz that a single term formula of the Drude type represents the refractive indices in that region reasonably well and also uniquely. This absorption term represents the weighted mean of the dispersion frequencies in respect of the particular region of the spectrum covered by the data. Naturally the weighted mean of the dispersion frequencies would not be the same for a different part of the spectrum, say the near

ultra-violet or the remote ultra-violet. In the latter cases, the longer absorption wave-lengths would play a more important part and the mean dispersion frequency would therefore appear to shift towards the visible spectrum.

Table I shows that the following formulæ fit the refractive index data of Rinne and Kolb at 23° C.

$$\left.\begin{aligned} n_\omega^2 &= 1 + \frac{1{\cdot}35159\,\lambda^2}{\lambda^2 - 92{\cdot}5^2} \\ n_e^2 &= 1 + \frac{1{\cdot}37863\,\lambda^2}{\lambda^2 - 92{\cdot}5^2} \end{aligned}\right\} \qquad (3)$$

($\lambda$ in $m\mu$)

The same dispersion wave-length fits the ordinary and the extraordinary indices and the birefringence appears as a consequence of different oscillator strengths in the two directions.

TABLE I

| $\lambda$ in $m\mu$ | $n_\omega$ (cal.) | $n_\omega$ (obs.) | $n_e$ (calc.) | $n_e$ (obs.) |
|---|---|---|---|---|
| 434·047 | 1·5543 | 1·5540 | 1·5634 | 1·5634 |
| 466·8 | 1·5514 | 1·5514 | 1·5605 | 1·5608 |
| 486·133 | 1·5500 | 1·5500 | 1·5590 | 1·5593 |
| 495·75 | 1·5493 | 1·5494 | 1·5584 | 1·5587 |
| 517·27 | 1·5480 | 1·5481 | 1·5570 | 1·5574 |
| 588·997 | 1·5446 | 1·5446 | 1·5536 | 1·5537 |
| 627·8 | 1·5432 | 1·5431 | 1·5522 | 1·5522 |
| 656·278 | 1·5424 | 1·5423 | 1·5513 | 1·5513 |
| 687·2 | 1·5416 | 1·5414 | 1·5505 | 1·5504 |
| 718·9 | 1·5409 | 1·5405 | 1·5495 | 1·5498 |

Sosman has given the most probable values of the refractive indices at 18° C. Table II shows the fit of these refractive indices for wave-lengths between 250·329 $m\mu$ and 410·174 $m\mu$ according to the formulæ

$$\left.\begin{aligned} n_\omega^2 &= 1 + \frac{1{\cdot}3500\,\lambda^2}{\lambda^2 - 92{\cdot}5^2} \\ n_e^2 &= 1 + \frac{1{\cdot}3786\,\lambda^2}{\lambda^2 - 92{\cdot}5^2} \end{aligned}\right\} \qquad (4)$$

It is seen that the same dispersion frequency as in (3) holds good in this region also. The strength of the extraordinary is very nearly the same in (3) and (4) but the strength of the ordinary shows a slight difference in (3) and (4).

TABLE II

| λ in mμ | $n_\omega$ (calc.) | $n_\omega$ (obs.) | $n_\epsilon$ (cal.) | $n_\epsilon$ (obs.) |
|---|---|---|---|---|
| 250·329 | 1·6003 | 1·6003 | 1·6114 | 1·6114 |
| 303·412 | 1·5775 | 1·5770 | 1·5874 | 1·5872 |
| 325·253 | 1·5712 | 1·5709 | 1·5808 | 1·58095 |
| 358·68 | 1·5640 | 1·5639 | 1·5738 | 1·5737 |
| 396·848 | 1·5581 | 1·5581 | 1·5677 | 1·5677 |
| 410·174 | 1·5564 | 1·5565 | 1·5660 | 1·5661 |

Differentiating the dispersion formulæ with respect to the temperature $t$ we get

$$\frac{dn_\omega}{dt} = -\frac{\gamma(n_\omega^2 - 1)}{2n_\omega} + \frac{1}{n_\omega}\frac{k_\omega \lambda^4}{(\lambda^2 - \lambda_r^2)^2}\chi_r$$

$$\frac{dn_\epsilon}{dt} = -\frac{\gamma(n_\epsilon^2 - 1)}{2n} + \frac{1}{n_\epsilon}\frac{k_\epsilon \lambda^4}{(\lambda^2 - \lambda_r^2)^2}\cdot\chi_r,$$

where $\gamma$ = coefficient of cubical expansion and $\chi_r = \frac{1}{\lambda_r}\frac{d\lambda_r}{dt}$.

Using these formulæ and the data of Radhakrishnan and Barbaron, $\chi$'s for different temperatures and wave-lengths have been calculated and tabulated in Table III.

TABLE III

$\chi \times 10^5$

| Temp. Range °C. | λ=253·7 mμ | | λ=365 mμ | | λ=546 mμ | | λ=589 mμ | | Author |
|---|---|---|---|---|---|---|---|---|---|
| | Ord. | Extra. | Ord. | Extra. | Ord. | Extra. | Ord. | Extra. | |
| − 200 to − 150 | | | | | 0·2 | 0·1 | | | Barbaron |
| − 150 to − 100 | | | | | 0·5 | 0·45 | | | do |
| − 100 to − 50 | | | | | 0·7 | 0·60 | | | do |
| − 50 to + 0 | | | | | 0·82 | 0·76 | | | do |
| 0 to + 50 | | | | | 1·0 | 0·96 | | | do |
| | 1·25 | 1·14 | 1·1 | 1·0 | 1·1 | 0·96 | 1·00 | 0·91 | Radhakrishnan |
| 50 to 100 | 1·4 | 1·31 | 1·3 | 1·15 | 1·2 | 1·1 | 1·14 | 1·07 | do |
| 100 to 150 | 1·5 | 1·39 | 1·34 | 1·27 | 1·3 | 1·2 | 1·23 | 1·10 | do |
| 150 to 200 | 1·6 | 1·47 | 1·4 | 1·33 | 1·4 | 1·29 | 1·33 | 1·16 | do |
| 200 to 250 | 1·68 | 1·59 | 1·55 | 1·4 | 1·45 | 1·35 | 1·44 | 1·2 | do |
| 250 to 300 | 1·77 | 1·69 | 1·63 | 1·44 | 1·53 | 1·5 | 1·53 | 1·3 | do |
| 300 to 350 | 1·86 | 1·8 | 1·7 | 1·51 | 1·64 | 1·56 | 1·58 | 1·42 | do |
| 350 to 400 | 1·98 | 1·87 | 1·8 | 1·62 | 1·72 | 1·63 | 1·69 | 1·5 | do |

From Table III we see that $\chi$ increases steadily with temperature. It is also noticed that $\chi$ approaches zero at very low temperatures. Ramachandran[10] has shown in the case of diamond and Radhakrishnan[11] in the case of quartz and vitreous silica that the value of $\chi$ tends to zero for very low temperatures.

Theoretically, the $\chi$ calculated for different wave-lengths should be the the same. Actually, we notice that it shows a systematic, though slight increase with decreasing wave-length. This apparent increase with decreasing wave-lengths can be explained as follows. The dispersion formula which is used in these calculations assumes a single absorption wave-length with an appropriate weight to represent the indices in the particular region. But when we move from one part of the spectrum, say from the visible to the near ultra-violet, the absorption wave-lengths having longer wave-lengths would become more effective than the rest, and the weighted mean of the absorption wave-lengths would therefore register an increase. The $\chi$'s of all the absorption wave-lengths would also be generally not the same, Normally, it might be expected that the longer absorption wave-lengths would have a greater $\chi$. Hence, the effective $\chi$ should show an apparent increase.

We also notice that the value of $\chi$ evaluated for the ordinary ray comes out slightly higher than that for the extraordinary. This may be explained as follows. The birefringence is a consequence of the same absorption wave-lengths having different oscillator strengths in the two principal directions. If the strengths of the deeper terms are larger for extra-ordinary than for the ordinary, the effective $\chi$ will be smaller for the former. The value of $\chi$ as calculated above using a single term dispersion formula would then come out as larger for the ordinary ray than for the extraordinary one.

The comparison of the thermo-optic behaviour of quartz and vitreous silica is very interesting. Vitreous silica has a negligible coefficient of thermal expansion and hence the refractive index shows a continuous increase with temperature quite similar to the positive part of the temperature variation of the refractive indices of quartz. A single term dispersion formula with the same dispersion wave-length as in quartz fits the refractive indices of vitreous silica in the same region of the spectrum. The formula at 18° C. is

$$n^2 = 1 + \frac{1{\cdot}0994\,\lambda^2}{\lambda^2 - 92{\cdot}5^2}$$

The $\chi$ can be calculated as above, and we again find a close parallelism between the behaviour of quartz and vitreous silica.

TABLE IV

$\chi \times 10^6$

| Temp. Range °C. | Vitreous silica | Quartz (approx.) |
|---|---|---|
| −160 to 18 | 0·8 | 0·7 |
| − 64 to 130 | 1·1 | 1·1 |
| 18 to 235 | 1·3 | 1·25 |
| 130 to 365 | 1·5 | 1·5 |
| 235 to 475 | 1·63 | 1·7 |

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## 4. SUMMARY

The temperature variation of the refractive indices of α-quartz contains a positive part, though it is completely submerged by the predominant negative part due to the thermal expansion. At the α-β transition temperature of 573° C., the structural changes represented by the α-β transformation cause a change in a direction opposite to that of the density change, *i.e.*, an increase in the refractive indices. The rate of change of the electronic dispersion wave-lengths decreases with decreasing temperatures tending to zero at very low temperatures. The thermo-optic behaviour of quartz and vitreous silica bear a close resemblance, the difference in the two cases being due to the difference in the thermal expansions.

## REFERENCES

1. Sosman .. *The Properties of Silica*, 1927.
2. Micheli .. *Ann. d. Phys.*, 1902, 7.
3. Rinne and Kolb .. *Neues. Jahrb. Min.*, 1910, **2**, 138–58.
4. Radhakrishnan .. *Proc. Ind. Acad. Sci.*, 1951, **33 A**, 22.
5. Barbaron .. *Compt. Rendus*, 1948, **226**, 1443.
6. Pockels .. *Ann. d. Physik. u. Chem.* (Wiedemann), 1889, **37**, 269–305.
7. Sosman .. *The Properties of Silica*, 1927, 748.
8. Radhakrishnan .. *Proc. Ind. Acad. Sci.*, 1951, **33 A**, 22; 1948, **27 A**, 44; 1947, **25 A**, 382.
9. Chandrasekhar .. *Ibid.*, 1951, **34 A**, 275.
10. Ramachandran .. *Ibid.*, 1947, **25 A**, 266.
11. Radhakrishnan .. *Ibid.*, 1948, **27 A**, 44.

# THE OXIDATION OF HYDROGEN SULPHIDE BY POTASSIUM IODATE

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Dean[1] studied the oxidation of sulphides with potassium iodate and found that the amount of sulphur oxidised to sulphuric acid depended on the concentration of the hydrochloric acid employed. Iodine monochloride appeared to be the actual oxidant and when the concentration of the acid was sufficient to prevent the hydrolysis of iodine monochloride, the sulphur was quantitatively oxidised to sulphate.

Our preliminary experiments showed that as in the case of chloramine-T[2] the products formed by the oxidation of hydrogen sulphide by potassium iodate were sulphur and sulphate, depending upon the pH of the system. The experiments were carried out in buffers having a pH sufficiently high as not to liberate iodine from iodate, on addition of potassium iodide. At lower pH values, the oxidation of hydrogen sulphide by iodate would be complicated by the reaction of hydrogen sulphide with the iodine liberated from iodate in an acid medium, in presence of iodide, formed by the reduction of iodate. The lowest pH employed was 7·0 at which there was no liberation of iodine by any reaction between iodate and iodide.

Iodate was always used in excess, and the oxidant left over after the complete removal of hydrogen sulphide, was estimated iodometrically.

The experimental technique of study of the oxidation of hydrogen sulphide was the same as that employed in the case of the reaction between the gas and chloramine-T[2].

0·1 N potassium iodate solution was prepared from A.R. potassium iodate.

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* This investigation was conducted at Central College, Bangalore, and formed part of the thesis of A. R. Vasudeva Murthy accepted for the M.Sc. Degree of the Mysore University.

## EXPERIMENTAL RESULTS

### TABLE I

*Reaction between Hydrogen Sulphide and Potassium Iodate*

| Sl. No. | pH solution | Buffer used* | Value of '*a*'† | Value of '*b*'‡ | Ratio of *b* to *a* |
|---|---|---|---|---|---|
| 1 | 7·0 | Phosphate—borax | 2·69 | 5·43 | 2·02 |
| 2 | 7·0 | Phosphate—borax with 0·1 N potassium iodide | 5·77 | 1·41 | 0·25 |
| 3 | 7·0 | Phosphate—borax + osmic acid | 5·16 | 1·88 | 0·36 |
| 4 | 7·0 | Phosphate—borax + brucine | 5·1 | 1·8 | 0·36 |
| 5 | 7·0 | Posphate—borax + 2 ml. of 5% sodium molybdate | 5·61 | 1·62 | 0·33 |
| 6 | 9·2 | Borax | 4·4 | 3·9 | 0·88 |
| 7 | 11·7 | Phosphate—Sodium hydroxide | 5·44 | 1·86 | 0·33 |
| 8 | 11·7 | Phosphate—Sodium hydroxide with 0·1 N potassium iodide | 6·5 | 0·86 | 0·13 |

† *a* = Volume of hydrogen sulphide (at N.T.P.) oxidised to sulphur and water.

‡ *b* = Volume of hydrogen sulphide (at N.T.P.) oxidised to sulphuric acid.

* The composition of the buffers was as indicated in *Hydrogen ions*, by Britton, 3rd Edn., Vol. I, p. 300, 1942.

### TABLE II

*Redox Potentials of Potassium Iodate—Potassium Iodide Systems*

| Sl. No. | pH | Buffer | System | Electrode | Redox potential in volts. |
|---|---|---|---|---|---|
| 1 | 7·0 | Phosphate—borax | Potassium iodate—iodide | Platinum bright | 0·557 |
| 2 | 7·0 | do | do + osmic acid | do | 0·557 |
| 3 | 7·0 | do | do | Platinum black | 0·557 |
| 4 | 7·0 | do | Potassium iodate—iodide + a crystal of iodine | Platinum bright | 0·557 |
| 5 | 7·0 | do | Potassium iodide—iodine | do | 0·557 |
| 6 | 9·2 | Borax | Potassium iodate—iodide | Platinum bright | 0·335 |
| 7 | 9·2 | Borax | do | Platinum black | 0·335 |
| 8 | 11·8 | Phosphate—sodium hydroxide | do | Platinum bright | 0·299 |
| 9 | 11·8 | do | do +osmic acid | do | 0·299 |

## Discussion

As stated in an earlier paper, dihydrogen sulphoxide appears to be the primary product of oxidation of hydrogen sulphide.[2] The sulphoxide can simultaneously undergo two reactions:

A decomposition (Reaction A) and an oxidation (Reaction B).

$$H_2SO \rightarrow H_2O + S \text{ (Reaction A).}$$

$$H_2SO \rightarrow H_2SO_4 \text{ (Reaction B).}$$

Examination of Table I indicates that the presence of potassium iodide considerably diminishes the production of sulphate both at pH 7·0 and pH 11·7. The oxidation potential of potassium iodate is greatly reduced by the presence of potassium iodide as shown in Table II. The rate of oxidation of the hydrogen sulphoxide to sulphate is thus diminished and the decomposition of the sulphoxide to sulphur therefore, takes place to a greater extent. Osmic acid and brucine, as in the case of chloramine-T, diminish sulphate formation. The molybdate also seems to diminish sulphate formation while in the case of chloramine-T, it considerably accelerates the production of sulphate. It is therefore to be concluded that catalysts have specific influence on the two simultaneous reactions undergone by dihydrogen sulphoxide.

Redox potentials were measured in the same way as in the case of chloramine-T. The results are given in Table II.

It is found that when 0·1 N potassium iodide and iodine are present in the solution along with iodate (0·1 N), the potential is the same as that of a solution having 0·1 potassium iodide and iodine only. It is also noticed that osmic acid does not affect the potential though it alters the relative proportions of sulphate and sulphur produced, during the oxidation of hydrogen sulphide by the iodate, at pH 7·0.

## References

1. S. Dean .. *J. Am. Chem. Soc.*, 1918, **40**, 619.
2. A. R. V. Murthy and B. Sanjiva Rao .. "Oxidation by Chloramine-T. Part I. Reaction between Hydrogen Sulphide and Chloramine-T," *Proc. Ind. Acad. Sci.*, 1952, **35A**, 7.

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